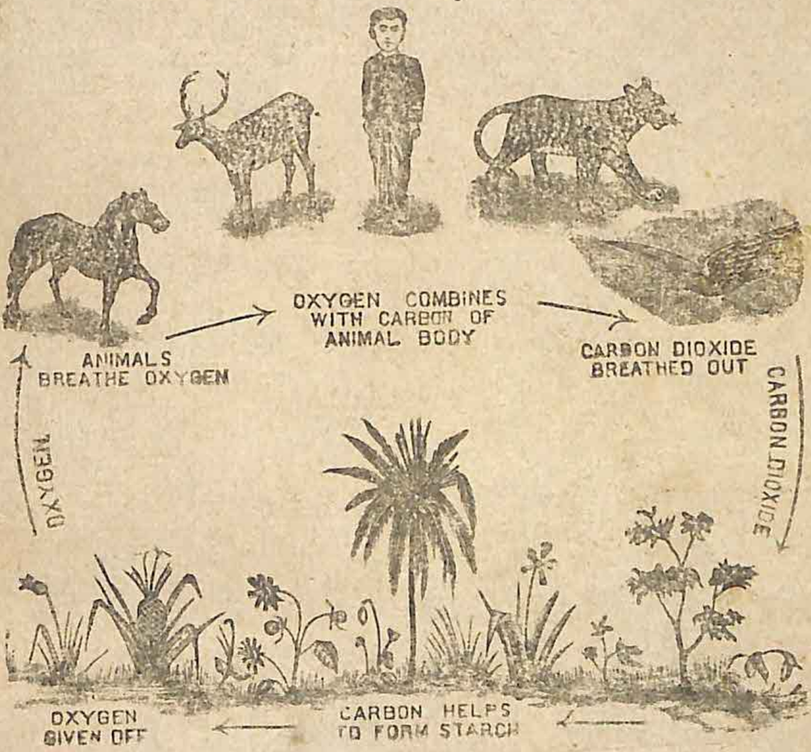
A TEXT-BOOK
OF
CHEMISTRY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OXYGEN GIVEN OFF
OXYGEN
ANIMALS BREATHE OXYGEN

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A TEXT BOOK
OF
CHEMISTRY

8795

[PRE-UNIVERSITY COURSE]

STATE INSTITUTE OF EDUCATION
Govt. of West Bengal

By

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SEVENTH EDITION
(*Thoroughly revised & Enlarged*)

August, 1970

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PREFACE

This text written for use in the Pre-University Chemistry course of the Indian Universities is based primarily on the admirable text book of INORGANIC CHEMISTRY written by Prof. L. M. MITRA and as such can lay claim to some of its distinctions which have made the original book so popular with students and teachers alike throughout India and abroad.

Prof. Mitra's text book is meant primarily for intermediate students of the Indian Universities and hence may seem rather too advanced for Pre-university students.

With the introduction of the Pre-University course followed by Three Years Degree course, it is now felt necessary (and there have been persistent requests from diffrent quarters also) to recast Prof. Mitra's Chemistry in accordance to the Pre-University syllabii of different Indian Universities so that the future generations of students may derive some of its benefits.

As a former student and later a colleague of Late Prof. Mitra, I have ventured to undertake the task. In so doing, I have tried to follow the original text as far as possible ; but I have not at the same time hesitated to deviate from such a course whenever such a departure, I have considered, would make the book more useful to those for whom it is meant.

Many new facts have been incorporated and several portions modernised in order to bring the book in line with the present day concepts of chemistry.

The organic portion is entirely written by me for which the responsibility is exclusively mine.

It is hoped that the book will be found useful as a text book for students reading in the Pre-University classes of different Indian Universities.

Criticisms and suggestions from readers are earnestly requested. They will receive our most serious attention and will be given effect to as far as possible in the next edition.

BANGABASI COLLEGE
Calcutta
The 8th. July, 1960.

S. K. Basu

PREFACE TO THE SECOND EDITION

It is a matter of great satisfaction to us that the book in its present form has been able to retain at least partially the popularity of the original one, which has enabled us to bring out the second edition of the book so soon after its first publication. We take this opportunity to express our heart-felt gratitude to our friends and colleagues in the different Colleges for their kind patrônage.

Time did not permit me and I did not also consider it necessary at this stage to undertake an elaborate revision of the book. I am, moreover, awaiting suggestions and criticisms from the readers which, I am sure, will prove of great help to me in revising the book for the next edition.

The few misprints which unfortunately crept in the first edition inspite of our best care have been rectified as they came to our notice. Minor alterations have been made here and there for the sake of greater lucidity. Some errors may still remain undetected. I shall feel obliged if the readers bring them to my early notice.

BANGABASI COLLEGE
Calcutta
The 1st. September, 1960.

S. K. Basu

PREFACE TO THE SIXTH EDITION

In the present edition, the text has been thoroughly revised and many portions enlarged and rewritten to conform to substantial changes introduced recently in the syllabii of the Pre-University course of different Indian Universities. While revising the text, I have also kept in view the marked changes in the nature of questions that are now being set in examinations of different Universities.

I hope, this book will continue to enjoy the popularity which has been extended to it ever since its publication by the students and teachers alike.

Suggestions and criticisms are cordially invited from readers for the improvement of the book.

BANGABASI COLLEGE
Calcutta
The 1st September, 1967.

S. K. Basu

SYLLABUS IN CHEMISTRY

FOR

PRE-UNIVERSITY COURSE

CALCUTTA UNIVERSITY

Theoretical

A concise treatment of essential points would be all that is required.

There shall be one paper (Theoretical) of 75 marks and of 3 hours duration.

CHEMISTRY

The course shall comprise :—

THEORETICAL

A concise treatment of essential points would be all that is required.

GENERAL

1. Common Laboratory Processes ; filtration, crystallisation, sublimation, distillation.

Solution-solubility—true solution and colloidal solution (elementary ideas).

2. Physical and chemical changes ; Law of conservation of mass.
3. Laws of chemical combination (by weight), Dalton's Atomic Theory.
4. (a) Application of Boyle's Law and Charles' Law.
   (b) Gay Lussac's Law of Gaseous Volume.
   (c) Avogadro's Law ; simple deductions ($M=2D$; diatomicity of elementary gas molecules) ; derivation of formulae from composition of water, hydrogen chloride and carbon dioxide.
   (d) Atomic weight, Molecular weight, gram-molecule.

5. Symbols, formulae and equations. Simple calculations on weights and volumes.

6. Equivalent weight and its determination ; Mg, Cu and Ag only ; Valency.

7. Ionic dissociation. Electrolysis—Faraday's Laws and simple calculations on $W=CZt$.

8. Brief but broad outline of atomic structure : Protons, electrons and neutrons; atomic number.

9. Acids, bases and salts—acidimetry and alkalimetry. Simple problems on the subject matter of the Course.

NON-METALS

1. Laboratory preparation of oxygen, hydrogen, nitrogen and carbon dioxide and their main properties and uses.
2. Oxidation and reduction. One method of preparation of hydrogen peroxide ; its properties, uses.
3. Catalysis. Allotropy referred to oxygen, cārbon and sulphur (names only).
4. Water : sources, hardness and its removal.
5. Air : proportion of oxygen and nitrogen by volume (Lavoisier's experiment).
   (a) Ammonia—Laboratory method of preparation ; outline of Haber's method, properties, uses.

(*b*) Nitric acid, (*i*) Preparation from nitrate, (*ii*) from ammonia (outline only), action on sulphur, sulphur dioxide, magnesium, zinc and copper ; properties of Acqua Regia.

6. Phosphorus—two main forms and their properties ; their uses—outline of preparation of phosphoric acid and phosphorus from bone ash.

7. (*a*) Laboratory preparation of chlorine, bromine and iodine ; their common properties ; uses.

(*b*) Preparation of hydrochloric acid in the laboratory—properties.

8. (*a*) Sulphuretted hydrogen—laboratory preparation ; properties and uses as reagent.

(*b*) Sulphur dioxide ; laboratory preparation—properties, uses. Outlines of manufactures of sulphuric acid by Contact and Chamber process (only raw materials, equations and conditions to be stated).

Uses of sulphur dioxide and sulphuric acid.

Alums—Potash alum and its uses.

Chemistry of Carbon Compounds :

1. Destructive distillation of coal and wood (without technical detail).

2. Hydrocarbons ; Saturated : Methane.
Unsaturated : ethylene, acetylene.
Aromatic : benzene.

Only sources, outline of preparation with equation, important reactions and uses.

3. One simple method of preparation : main properties and uses of the following classes of organic compounds with special reference to the compound noted against each :

(*i*) Alcohol (ethyl alcohol).
(*ii*) Aldehyde (acetaldehyde).
(*iii*) Ketone (acetone).
(*iv*) Carboxylic acid (acetic acid, oxalic acid and citric acid).
(*v*) Ester (ethyl acetate).
(*vi*) Halogen (derivative choroform).

METALS

1. Occurrence, outline of extraction without any technical details, properties and uses of—zinc, aluminium, sodium and iron.

2. Preparation (in outline) and use of—
(*i*) Solvay's sodium carbonate.
(*ii*) Caustic Soda (Castner's).
(*iii*) Lime.
(*iv*) Bleaching powder.
(*v*) Copper Sulphate.
(*vi*) Plaster of Paris.

PRACTICAL

25 MARKS

1. Fitting up of a simple apparatus, *e.g.*, a wash bottle.

2. Separation of the ingredients of a solid mixture by solution, filtration, crystallisation and sublimation.

3. (*a*) Preparation and study of the properties of oxygen, carbon dioxide, ammonia.

(*b*) Study of the action of Sulphuretted hydrogen on different salt solutions.

4. Identification of—

(*i*) Acidic radicals (chloride, carbonate, nitrate and sulphate) in sodium, potassium or ammonium salts.

(*ii*) Basic radicals (copper, aluminium, iron, zinc, calcium and magnesium) given singly in compounds soluble in water or dil. hydrochloric acid.

5. Titration of acids and bases using methyl orange or phenophthalein indicators.

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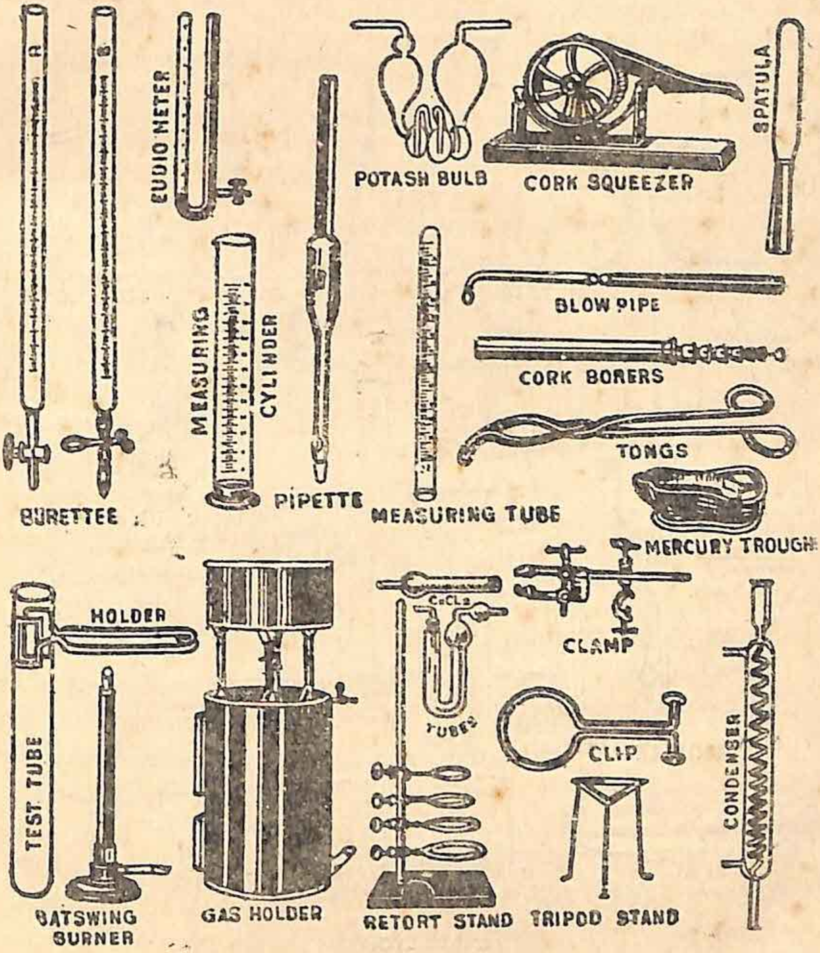
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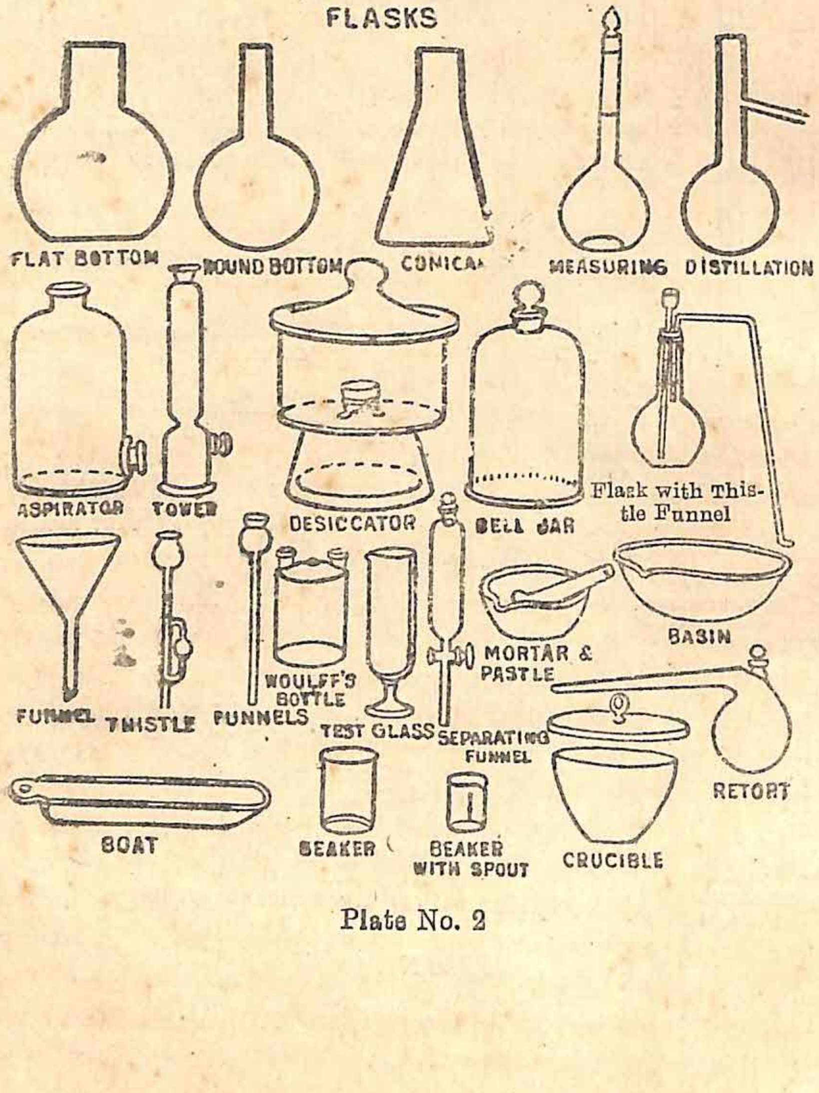
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CRUCIBLE

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A TEXT-BOOK OF CHEMISTRY

CHAPTER I

INTRODUCTION

Chemistry being one of the branches of science, it is only prope that we should enquire: "What is science ?" "What are its aim and methods ?"

Although Science is founded on and embraces the whole realm o human knowledge, the multitude of knowledge gathered as isolate facts is not science any more than bricks are houses ; though fact are as essential for building the edifice of science as bricks are fo houses. The amorphous mass of unconnected facts must be properl arranged, classified and systematized before it can deserve the titl of science.

Science is, therefore, defined as knowledge classified, correlated an organized into a system.

A man of science works by the following steps :—

(1) He starts by collecting facts by careful observations an experiments. In collecting facts, he must not be influenced by hi personal likes and dislikes and try to avoid all possible sources c errors.

(2) Having collected impartial and accurate facts about som phenomenon, he compares and sorts them out and then tries to discover some underlying relations existing between these apparentl unconnected facts. Thus he often discovers a common principl unifying them. The statement of this unifying principle constitute a **rule** or **law**.

(3) He now makes guesses or assumptions for what he can no see or directly prove to account for these facts. These assumptio are known as a **hypothesis**.

(4) A fruitful hypothesis should suggest new experiments to b tried and these experiments lead to newer facts. If the experiment prove the validity of the hypothesis, then it becomes a **theory**. I not, the hypothesis, has to be modified or totally rejected in favou of a new one.

A further discussion given below will elucidate more fully th precise meanings of the terms facts, hypothesis, theory and law.

Facts are direct appeals to physical perception. They are capable of bei perceived by our senses, and are demonstrable by actual experiment or observatio Thus the statement 'a piece of dry wood burns more easily than a piece of wet woo

—is a fact, for we can prove it by actual experiment. The *aim* of science is to explain facts. Now, if we are asked—'Why does a piece of dry wood burn more easily than a piece of wet wood ?' We are asked to explain the above fact ; and we try to explain it by means of a supposition or *hypothesis*. Our answer to the above question *may* be, 'wet wood does not readily burn, for the temperature required to start the burning is not easily attained due to the cooling effect of evaporation of water from the wet wood'. This hypothesis may be correct, as far as it goes. When a *hypothesis* has been tested, as far as possible, and is not found wanting, it then grows up into a *theory*.

A *law* in science implies generalization deduced from experimental facts. It is a statement describing some general facts or some constant mode of behaviour.

Laws are only true so long as no facts in conflict with them are known.

A hypothesis is a speculative term ; it is an assumption which goes *beyond* the observed facts ; while a law is a generalization which does not go beyond the observed facts.

Science is based on experiments. Experiments are first performed ; keen observations are now made about them ; and then inferences are drawn from these observations. *To infer is to find out what will be true if something else is true.* The inference may be embodied in the form of a hypothesis or a theory. We usually reason it out ; and reasoning means *getting some knowledge from other knowledge.*

Branches of Science.—The realm of science embraces the whole field of human knowledge which has grown so vast in recent years that it has become impossible for any human mind to comprehend it in its entirety. So science has been divided artificially into several departments for the convenience of study and these compartments constitute different branches of science. Science has been divided into *abstract* and *concrete sciences*. Abstract sciences, *e.g.* mathematics, logic and philosophy are really methods of classifying and investigating facts presented by other branches of science.

The concrete sciences deal with phenomena which can be investigated through our senses. There are two broad divisions of concrete sciences, namely the *physical* sciences and *biological* sciences. The physical sciences, for example, *physics* and *chemistry* deal with inorganic phenomena, *i.e.* with the nature of matter and energy while biological sciences, for example, *botany*, *zoology* and *physiology* deal with organic phenomena, *i.e.* phenomena connected with living processes.

Definition, scope and aims of Chemistry.—What is chemistry ? The science of chemistry deals with the properties and composition of different kinds of matter and particularly studies those changes which affect the internal structure of a matter transforming it into another of altogether different kind. These changes are known as chemical changes. Chemistry studies the conditions and the mechanisms by which these changes are brought about. So a man, versed in the knowledge of chemistry, by devising proper conditions can cause regulated changes to occur in matters endowing them with new sets of useful properties. Thus through chemical knowledge, coal has been turned into petrol and out of dirty looking coal tar, dyes of wonderful and varied colours have been prepared. From coal tar again, drugs possessing miraculous power of healing have been obtained. The wonder drug, penicillin and other antibiotics are gifts of chemical laboratories. By the manufacture of artificial manures, chemistry has made barren lands fertile and it is hoped chemistry would be able to help agriculture to solve the much vexed food problems of the world in near future.

Chemistry is sometimes abused for the discovery of dynamite and other high explosives, which through the evil genius of man have been responsible in the past for so much destruction and human sufferings in war. But we must remember that many of the engineering feats of today which have conferred untold benefits on humanity such as the construction of dams, tunnels, canals etc. would have remained unfulfilled dreams without them.

CHAPTER II

MATTER AND ENERGY

Matter.—Any kind of material in the world which has weight, occupies space and can be moved by a force is called matter. A particular kind of matter is called a substance.

A matter has got weight because of the pull of the earth on it. The pull of the earth is called gravity. Now the gravity of the earth is not the same everywhere. For example, as we go up, the gravity becomes less and a substance which is lifted high up in air losses a part of its weight though the matter contained in it, that is its mass, remains constant. So the mass of a substance must be distinguished from its weight which the substance possesses due to the pull of the earth. But as the pull of the earth (gravity) on a body varies directly as its mass, a body of two units mass weighs twice as much as a body of one unit mass. Hence the weight of a body is taken as a measure of its mass at any one place. A matter also occupies space. The bit of a space a matter occupies is called its volume.

Energy.—Heat, light, electricity, sound etc., are not matter. They are forms of energy. Energy is the ability to do work.

A piece of any metal, say a knife or a lead shot, is matter. It has the same weight whether hot or cold, stationary or in motion. But when hot or in motion, it has more energy because it can do more work. But the amount of extra energy does not go to increase the mass or the weight of the knife or the lead shot. Energy has no mass or weight.

One form of energy can be converted into another form of energy, for example, electricity may be converted into heat, light, sound etc. Until very recently, matter and energy were supposed to be not inter-convertible. But scientists of late have been able to release the energy locked within matter itself. This energy is produced when the nuclei of atoms split. A tiny bit of matter disappears and in its place an enormous amount of energy is produced. It has been calculated that a pound of any matter on complete annihilation can yield energy equal to that produced by the burning of 200,000,000 gallons of petrol.

The Three Fundamental Units.—In order to express quantity of matter an exact system of weights and measures are necessary. The choice of units is quite *arbitrary*. Some kinds of definite units have been agreed upon either by usage or by law or for the sake of convenience. In all scientific investigations the system of measurement employed is the *French* system, or the *Metric* system. In this system

(i) the *standard* unit of length is one **Metre.**
(ii) the *standard* unit of mass is one **Kilogram.**
(iii) the *standard* unit of time is one **Second.**

N. B.—A metre was *originally* defined by the French Republic (1808) as the *millionth part* of an arc of the earth measured along the meridian from the North Pole to the Equator, passing through Paris.

In the metric system sub-multiples of units are denoted by the Latin prefixes *deci* = one-tenth, *centi* = one-hundredth, *milli* = one-thousandth ; while the multiples are denoted by the Greek prefixes *deca* = ten, *hecto* = hundred, *kilo* = thousand.

The Unit of Length.—It is the **metre.** But for laboratory measurements centimetre, or one-hundredth of the metre, is taken as the unit. A **metre** is defined as the exact distance between two marks on a standard bar of platinum at 0°C, kept at the Archives in Paris.

1 Metre =	10 Decimetres	10 Metres	=	1 Decametre
=	100 Centimetres	100 ,,	=	1 Hectometre
=	1,000 Millimetres	1,000 ,,	=	1 Kilometre.

For small measurements, the metre is found to be rather big and not convenient. The *smaller* unit centimetre is used in such cases.

The Unit of Volume or Capacity.—It is the **litre.** But for the measurement of *small* volumes, one thousandth part of a litre, *viz.* cubic centimetre, is usually taken as the unit. A litre may be defined as the exact volume of a cube each face of which is a square decimetre. If now we divide a 'litre' into 1,000 equal parts, each is called a **cubic centimetre** (c. c.) or **millilitre** (ml.)

The Unit of Mass.—It is the **kilogram.** But for laboratory measurements the unit chosen is the **gram** (or **gramme**).

The standard kilogram is defined to be the mass of a certain lump of platinum kept at the Archives in Paris. A gram or gramme is one-thousandth part of the standard *kilogram*. Originally the gram was defined as the mass of 1 c. c. of distilled water at 4°C. Accurate measurements have shown that the two units are not exactly the same, and 1 gm. of distilled water at 4°C occupies a volume *slightly* greater than 1 c. c. (1·000027 c. c.).

For ordinary purposes we may define it thus :—**A gram is the mass of one cubic centimetre of distilled water at 4°C** (*i.e.* at the maximum-density point). The fractions and multiples of a gram are :

1 Gram = 10 Decigrams
= 100 Centigrams
= 1,000 Milligrams

10 Grams = 1 Decagram
100 " = 1 Hectogram
1,000 " = 1 Kilogram.

The unit of time is called the **second.** It is the $\frac{1}{24\times60\times60}$th of a mean *solar day*.

The system in which **centimetre, gram** and **second** are taken as the units of **length, mass** and **time** respectively, is called the **C. G. S. system.**

Temperature.—The Centigrade scale of temperature is used universally in scientific works. On the Centigrade scale, the freezing point of water is taken to be 0°, while the boiling point of water at the standard pressure is taken to be 100°. The space between 0° and 100° is divided into hundred equal divisions, each being called a degree. There are two other scales—Fahrenheit and Reaumur, which are seldom used in scientific works. According to these scales, the freezing point of water is designated 32° and 0° and the boiling point 212° and 80° respectively, both the points being measured at standard pressure.

Relation between the three scales.—If C, F and R represent a particular temperature on the Centigrade, Fahrenheit and Reaumur scales respectively, then it can be proved very easily that—

$$\frac{C}{100}=\frac{F-32}{180}=\frac{R}{80}\ Or,\ \frac{C}{5}=\frac{F-32}{9}=\frac{R}{4}.$$

A simple method of converting Centigrade scale into Fahrenheit and vice versa are as follows :—

1. Add 40 to the given scale reading.

2. (*a*) To convert Centigrade degree into Fehrenheit, multiply the sum by $\frac{9}{5}$.

(*b*) To convert Fahrenheit into Centigrade multiply the sum by $\frac{5}{9}$.

3. Subtract 40 to get the reading on the other scale.

Problem. 1. Find the temperature in the Centigrade scale corresponding to 32°F.

Step 1. $32+40=72$
,, 2. $72 \times \frac{5}{9} = 40$
,, 3. $40-40=0°C$

2. Find the temperature in the Fahrenheit scale corresponding to $-40°C$

$$-40+40=0$$
$$0 \times \frac{5}{9} = 0$$
$$0-40=-40°F.$$

N.B.—At $-40°C$ the reading in the scales are the same.

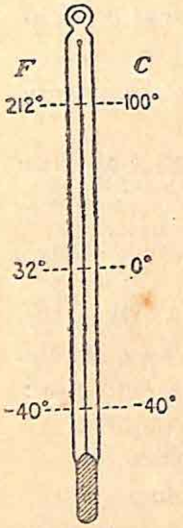

Fig. 1—Relation between the three scales

States of Matter—Matter can exist in three states, namely, solid, liquid and gas.

Solid—*A solid has a fixed volume and shape.*

Thus a gold coin, if carefully preserved, will retain both its volume and its shape after many hundred years.

Liquid.—*A liquid has a fixed volume, but no fixed shape.*

Thus 1 *pint* of milk, put inside a *gallon* jar or a *quart* bottle, does not change its volume. It is still one pint, But it takes up the shape of that part of the *gallon* jar, it is in contact with, when poured into the jar ; or the shape of the interior of the *quart* bottle, it occupies, when poured into the latter.

Gas—*A gas has no fixed volume or shape.*

Thus a small amount of a gas can fill both a big room and a small room. A gas never has any *surface* except that of the vessel containing it.

Matter, in general, is converted, by application of heat, into liquid state from solid, and by further application of heat, into gaseous state and the reverse change takes place on cooling.

Let us take the case of water. It is a liquid at the ordinary temperature. When cooled, it is converted into *solid* water, *viz.* ice : and when boiled, it is changed into *steam*. A solid is changed into liquid and a liquid into its vapour by *heat*. A reverse set of changes take place on *cooling*.

Properties of matter.—Again, different kinds of matter possess different *qualities* known as *properties*. *Thus*, ordinary sulphur is *pale yellow in colour, heavier than water, melting at 113° and boiling at 444°*. It is *insoluble* in water, but *readily dissolves* in carbon disulphide. It is a *non-conductor* of electricity. These qualities of sulphur are called the **specific physical properties** of Sulphur because they are characteristics of Sulphur. There is another characteristic property of Sulphur, *viz* it *burns* in air giving off sulphur dioxide gas which possesses a sharp smell. It is known as the **specific chemical property** of sulphur; for here we get a *new substance*, *all* these specific properties (both *physical* and *chemical*) of which are different from those of sulphur. Similar is the case *with any other* substance.

Molecular Constitution of Matter.—Furthermore, matter is regarded by the Chemists and Physicists as being composed of minute particles. Every substance, whether solid, liquid or gas, presents the appearance of a vast number of extremely minute particles. To these particles the name 'molecules' (or little masses) has been given. We can try to have some idea of these molecules if we suppose a body to be divided and subdivided into smaller parts. Let us take the case of *chalk*. It is a compound of three different elements carbon, calcium and oxygen. If we go on dividing and subdividing a piece of chalk, we shall certainly reach at a point when any further subdivision will break it up into the elements carbon, calcium and oxygen. If, at least in imagination, we can stop exactly at the point when it has reached the final stage, so that it still retains the properties of chalk and the next step will break it up into the elements, we may then suppose to have come to the 'molecule' of chalk.

Def. of Molecule.—A molecule is the smallest particle of any kind of matter, element or compound which can exist in the free state and can still preserve the character of that kind of matter.

The molecules of any particular substance are all alike; the molecules of different substances are different. Thus in sulphur the molecules are all of one kind, while in water they are all of another kind. The chemical properties associated with sulphur are the properties of the individual Sulphur molecules, while those belonging to water are the properties of the molecules of water. *The properties of a substance, therefore, are the properties of its molecules.*

Atoms.—Though matter is supposed to consist of molecules, the molecules are not usually simple, indivisible masses but are themselves supposed to be made up of still smaller particles called atoms (Greek *a=not* ; *temno=I cut*).

Def. of Atom.—An atom is the smallest particle of an element which can take part in a chemical change.

An atom is no longer considered to be the smallest indivisible particle of an element. It is now definitely known that an atom is made up of still finer particles—protons, electrons etc. The structure of an atom will be discussed in a later chapter.

Physical and Chemical Changes.

Matter is capable of undergoing a variety of changes some of which are called *physical changes* and the others *chemical changes.*

Physical changes *are those changes which alter some of the specific properties like the state of aggregation, texture, electrical or magnetic condition etc., of matter without bringing about any change in the composition or condition of its molecules.*

The original molecules remain unaltered. No new molecules are formed as a result of a physical change.

Illustrations :—

(*a*) When water is boiled, it is converted into steam ; and When water is cooled, it changes into ice. These are physical changes, for the molecules of ice, water and steam have the same composition.

(*b*) A piece of steel when rubbed with a magnet comes to possess the peculiar property of attracting small pieces of iron. This change is physical, for no *new* substance is formed when iron is magnetized.

(*c*) When a piece of platinum wire is strongly heated, it first becomes red-hot and afterwards white-hot. It then gives out light. When heating is discontinued and the wire is consequently cooled, we find that it has lost its property of giving out light although it is *still* platinum. The change is only physical.

Chemical changes *are those changes which alter the specific properties of matter by bringing about a change in the oomposition or constitution of its molecules.* Altogether new molecules are formed as a result of a chemical change.

Illustrations :—

(*a*) When an electric current is passed through acidulated water, the latter is decomposed into two gases, hydrogen and oxygen. This is a chemical change, for we get altogether *new* molecules.

(*b*) When a candle burns, a portion of the wax melts—this is a physical change ; but a greater portion of it is converted into carbon dioxide and water. This latter, certainly, is a chemical change, for the molecules of wax are altogether different from those of both water and carbon dioxide.

(*c*) When a piece of iron is left exposed to air for a long time, it rusts. This is a chemical change.

Many chemical changes are constantly going around us in the familiar process of everyday life. The burning of a candle, the burning of coal, or when we take bread, meat, vegetable etc., whereby they are converted into flesh, bones etc., are examples of chemical changes.

Exothermic Compounds.—Chemical reactions in which heat is **evolved** are called *exothermic reactions e. g.* burning of coal. And when a compound is formed from its elements with the *evolution* of heat, it is called an *exothermic compound e.g.* carbon dioxide, water etc.

Endothermic Compounds.—Chemical reactions in which heat is **absorbed** are called *endothermic reaction.* And when a compound is formed from its elements with the *absorption* of heat, it is called an *endothermic compound e.g.*, acetylene, carbon disulphide, chlorine monoxide, nitric oxide etc.

Indestructibility of Matter.—We know that when water is boiled, it disappears ; when a candle burns, both the wick and the wax entirely disappear, and if the burning candle be placed on the pan of a balance, practically all its weight is lost. Again, a piece of magnesium wire, on being strongly heated in air, burns with a brilliant light and leaves a white residue, which, when weighed, will be found to be heavier than the piece of magnesium taken A big tree is found to grow out of a tiny seed.

When we try to follow these, we are confronted with some questions which naturally come to our mind. Is water actually destroyed ? Is there a destruction of the substance of which the candle is composed ? Whence does the additional weight to magnesium come ? Can matter be *created ?* We can certainly answer these questions one by one. When water is boiled, it only changes its state and is *not* destroyed. The candle loses weight, for the products of its combustion in the form of *colourless gases* are disappearing into the atmosphere. Magnesium gains in weight, for it unites with the oxygen of the air to give that white residue. The growth of a tree is due to the nutrition it receives from the air and the soil. As a matter of fact, Chemists have reasons to suppose that—**"In no chemical action is any kind of matter destroyed or created".**

This is the **Law of Conservation of Matter.** It may be briefly stated thus :

Matter is indestructible, and, consequently, the total quantity of matter in every chemical action is exactly the same after the change as the total quantity of matter befor the change.

The above law has been conclusively proved by the following experiments.

(i) **Charcoal Experiment.**—A round-bottomed flask is provided with a tightly fitting stopper, through which two stout copper wires are introduced. To the end of one of the wires is soldered a small capsule made of copper. A piece of charcoal is placed in the capsule, and a thin platinum wire, joining the two copper wires at their ends, is wound round it. The flask is now filled with oxygen by the displacement of air. The stopper is replaced and tightly fitted and the whole apparatus is very carefully weighed. Electric current is now passed through the platinum wire which becomes red-hot and the piece of charcoal burns away to carbon dioxide gas. At the end of the reaction, the whole apparatus is allowed to cool and weighed again. It is found that though the piece of charcoal has disappeared (only a little ash is left) and practically lost, the weight of the apparatus remains *unaltered.* The piece of charcoal has been transformed into the invisible gas, carbon dioxide. This proves the indestructibility of matter.

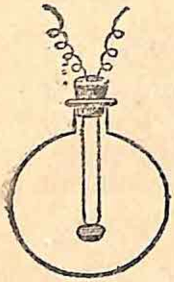
Fig. 2—Charcoal Expt.

(ii) **Landolt's Experiment.**—Landolt took solutions of ferrous sulphate and silver sulphate which would react together without the production of *much* heat, in two different arms of a H-shaped tube (fig. 3). The ends of the tube were next sealed to prevent the possibility of mechanical loss of materials. It was now weighed in a very sensitive balance, using counterpoise of the same size and shape. Then by tilting the vessel the solutions were carefully brought in contact with each other and the chemical change was allowed to take place. Silver sulphate was reduced to metallic silver by ferrous sulphate. After the reaction was over, the vessel was cooled and weighed in the same balance using the same counterpois. Landolt found that the weight remained practically unchanged.

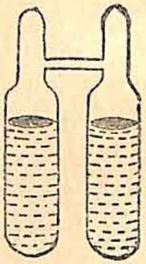
Fig. 3—Landolt's Experiment.

It is clear from the above experiments that there has been no *destruction* or *creation* of Matter, but merely a *redistribution.*

CHAPTER III

DIVISION OF MATTER : ELEMENTS AND COMPOUNDS

The various forms of matter may be divided into two broad classes :

Matter
Element
Compound

Element.—*An element is a substance which has not been resolved or split up by chemical analysis into two or more simple and dissimilar substances.* Examples of elements are :—hydrogen, oxygen, iron etc.

From the electronic point of view, by an element is meant a *substance which consists wholly of atoms having the same nuclear charge.*

Elements are of two kinds—*Metals* and *Non-metals*. We are familiar with many metals such as copper, iron, silver, gold, aluminium, tin, zinc etc. They possess a bright shine and lustre and are good conductors of heat and electricity. Metals can be hammered into thin sheets and drawn into wires.

Sulphur of which gun-powder is made and phosphorus which is used for making matches are typical non-metals lacking lustre and power to conduct heat and electricity. Other common non-metals are carbon, iodine, oxygen and nitrogen.

How the elements are met with in Nature.—Some of the elements are met with in nature in the *uncombined* (*i.e.*, *free* or *native*) state *e.g.*, oxygen and nitrogen in air ; gold, mercury etc in the crust of the earth ; and gold in sea-water. But most of the elements occur in the combined state (*i.e.*, in combination with other elements as compounds) *e.g.*, water-vapour and carbon dioxide in air ; silica, silicates etc. in the earth's crust , and common salt etc. in sea-water.

Distribution of the Elements.—Up till now *ninety-two* elements have been discovered in nature, only a limited number of which appears to be common and important elements. The following table will give *a rough* idea of the distribution of some of the elements in the **crust of the earth** to the depth of 24 miles, in sea-water and other water, and in air.

Oxygen	..	*about*	50%	Sodium	.. *about*	2·33%
Silicon	..	,,	26%	Potassium	.. ,,	2·33%
Aluminium	..	,,	7·23%	Magnesium	.. ,,	2·11%
Iron	..	,,	4·12%	Hydrogen	.. ,,	0·37%
Calcium	..	,,	3·18%	Carbon, Chlorine, etc.	*less than*	1%

In addition to elements found in nature, several elements have been made by nuclear scientists. These man-made elements have At. wts. greater than that of ura-

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N. B.—Boyle defined an element as '*the practical limit of Chemical Analysis*', *and* a substance '*incapable of decomposition by Chemical means*'.

nium and are known as Trans-uranium elements. One of them, plutonium, is manufactured in large quantities for the construction of atom bombs.

Elements are building blocks out of which other substances (compounds) are made of.

Compound.—*A compound is a substance out of which two or more essentially dissimilar substances can be obtained, and, as such, is formed by the union of two or more elements in definite proportions by weight.* Water, chalk, carbon dioxide etc. are examples of compounds.

Some Compounds of the present day were formerly known as elements.—Compounds like water, lime etc., were formerly regarded as elements; but the old view has changed as they have been split up into different substances.

The properties of a compound are not the same as the properties of the elements of which it is composed. Indeed, the properties are sometimes very different. For example, water, a liquid, is very much different from its constituent elements, hydrogen and oxygen, both of which are gas.

Water puts down fire while oxygen makes it burn all the more brightly.

Now two or more substances may be mixed together without the substances losing their individual properties when we have a *physical* or *mechanical mixture.*

Mixture.—*A mixture is formed by the mere blending of two or more elements or compounds in any proportion by weight, without union and without loss of their individual properties. The components of a mixture therefore, can be separated by easy mechanical means like solution, distillation etc.*

Distinction between a Mechanical Mixture and a Chemical Compound.

Mechanical Mixture	Chemical Compound
1. *In a mechanical mixture the properties of the components are retained i.e., the properties remain unchanged.*	1. *In a chemical compound the properties of the constituents are entirely changed; and the compound possesses properties entirely different from those of the constituents.*
(The properties of a substance are the properties of its molecules, and in a mechanical mixture the molecules of the ingredients remain unchanged).	(When a compound is formed from two or more ingredients, the molecules of the ingredients are changed, altogether *new* molecules are formed. These new molecules have properties different from those of the ingredients.)

Illustration.—Let us take **iron** (or more correctly *steel*) **filings** and powdered **sulphur.** We know that iron is attracted by a magnet. We shall see later on that iron dissolves in dilute sulphuric acid giving off hydrogen, and sulphur dissolves in carbon disulphide.

(A) We now thoroughly mix iron filings with powdered sulphur in a mortar. By doing so we find that all properties of iron and sulphur still exist in the mixture. Thus—(i) if we spread the above mixture on a paper and hold a bar magnet over it, iron particles are attracted by the magnet and sulphur particles are left on the paper ; (ii) if we treat a small amount of the mixture with dilute sulphuric acid, iron will dissolve but not sulphur, giving off an *odourless* gas, hydrogen , and (iii) if we take a little of the mixture in a test tube and shake it with carbon disuphide, sulphur will dissolve and iron filings will be left behind , (iv) the colour of the mixture is intermediate between black (of iron filings) and yellow (of sulphur particles).

(B) We next take a little of the mixture of iron filings and sulphur in *right proportion* by weight in a test tube and heat it strongly. Iron goes to combine chemically with sulphur. The resultant substance is a chemical compound, *viz.* **iron sulphide.** It now possesses properties altogether different from those of iron and sulphur. Thus—(i) when we hold a magent over the *powdered* iron sulphide, iron is not attracted , (ii) when we shake a small amount of it with carbon disulphide, sulphur does not dissolve , and (iii) when we treat it with *dilute* sulphuric acid, a new gas, possessing the *smell of rotten eggs*, is given off.

2. *The ingredients of a mechanical mixture can be separated from each other by easy mechanical means.*	2. *The constituents of a chemical compound cannot be separated by such mechanical means.*

Illustration.—Both iron and sulphur in a mixture of iron filings and sulphur can be separated by—(i) drawing a magnet over it, and (ii) by treating it with carbon disulphide. And both these methods are mechanical methods.

3. *No thermal change takes place in the preparation of a mechanical mixture.*	3. *The formation of a chemical compound, on the other hand, is always attended by a thermal change (i.e., heat is either evolved or is absorbed).*

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Illustration.—We go back to the case of **Iron filings** and powdered **sulphur.** When they are simply mixed together, there is neither absorption nor evolution of heat. A great deal of heat, however, is developed during the combination of iron and sulphur to form iron sulphide. This is more clearly shown by taking powdered **sulphur** and **zinc,** instead of iron filings. (i) We thoroughly mix powdered sulphur and zinc. There is no thermal change. We have got a mixture. (ii) we now heat only a portion of the mixture by allowing the flame of a Bunsen burner to play on it for a short time to *start* the reaction. Zinc and sulphur chemically react with almost explosive violence showing that much heat is developed.

N. B.—It must be noted that thermal, actinic (light) or electrical phenomena *usually* occur during a chemical reaction. Their absence means that the action is **not a chemical action.** A simple voltaic cell is the example of a chemical action attended by electrical phenomena.

4. *In a mechanical mixture the components may be present in any proportion by weight.*	4. *In a chemical compound, however, the constituents must be present in definite proportion by weight.*

Illustration.—Iron filings and powdered **sulphur** may be **mixed in any proportions by weight to** give a mechanical mixture. But in **iron sulphide,** the **proportions by weight of** iron and sulphur are **fixed.**

5. *A mechanical mixture is heterogeneous in character ; and may, sometimes, be homogeneous.*	5. *A chemical compound is always homogeneous and is never heterogeneous in character.*

Illustration.—Mixture of powdered sulphur and zinc, when seen through a microscope, shows that the two substances are lying *side by side* and is heterogeneous in character. Solution obtained by stirring common salt with water is, however, a homogeneous mixture. A *pure* chemical compound will *always* appear homogeneous when seen through a microscope or subjected to other tests.

Homogeneous substance.—A homogeneous substance is one of which any portion taken at random has got exactly the same composition and properties as in every other portion (—*Taylor*).

Heterogeneous substance.—A heterogeneous substance is one which shows different composition and properties in different parts of it.

N. B.—Distinctions 3 and 5 do not always hold good in the case of **solutions.**

CHAPTER IV

COMMON LABORATORY PROCESS

Many processes are carried out in chemical laboratories as a matter of daily routine. The students should make themselves familiar with these processes. Some of these processes are described below.

Sedimentation.—The method of allowing an insoluble heavy solid, mixed with a liquid, to settle at the bottom of the liquid is called **sedimentation** while the process of separating the liquid from the top without disturbing the sediment is called **decantation.**

Decantation.—This method consists in allowing an insoluble, heavy solid, *held in suspension* in a liquid, to settle at the bottom (*sedimentation*) and then carefully *pouring off as much of the clear supernatant liquid as possible.*

Filtration.—Another method of removing insoluble solid impurities present in a liquid is filtration. By this method the separation is effected *more completely* than in the other processes ; and insoluble solids, *both heavier and lighter than a liquid*, can be removed. The muddy water, for example, is allowed to pass through a *porous* substance (like *filter-paper*, *charcoal*, *cotton*, *canvas*, *unglazed porcelain*, *etc.*) which allows the liquid (together with anything that may remain dissolved it it) to pass through its pores, but not the insoluble solid substances, for they are too large to do so.

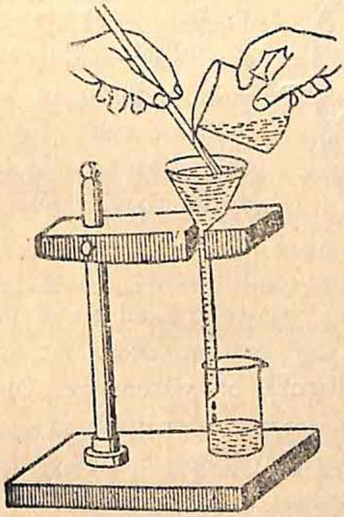

Fig. 4.—Filtration

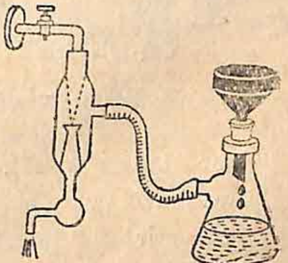

Fig. 5—Rap d filtration : Filter pump

In the laboratory, filtration is ordinarily effected by pouring the **liquid** down a glass rod into a circular piece of filter paper folded in the form of a cone and supported in a glass-funnel (fig. 4). The clear liquid that passes out of the filter-paper is called the **filtrate** ; while the insoluble solid substance left on the filter-paper is known as the **residue.**

Rapid Filtration.—For a rapid filtration in the laboratory, a filtering flask is used It is fitted by means of a rubber stopper, with a porcelain funnel having a perforated disk inside (*Buchner funnel*). The filter-paper is laid on the disk. The liquid, to be filtered, is poured on the funnel and the side-tube of the filtering flask is connected with a filter-pump (fig, 5) fixed to the water-tap. The tap is turned on. Water rushes out of the filter-pump when pressure inside the filtering flask is reduced with the production of partial vacuum and the atmospheric pressure readily drives the liquid in the funnel through the filter-paper. The process is also called *vacuum filtration* or *filtration under reduced pressure.* Again, note that hot solutions filter more rapidly than cold solution.

Hot-water funnel—It is a glass funnel put inside a double-walled copper funnel filled with water and provided with a slanting cylinder, closed at the bottom, which is heated in a Bunsen flame. The method prevents hot solutions from getting cooled during filtration (fig. 6).

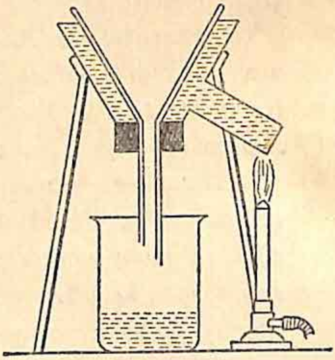

Fig. 6—Hot-water funnel

Industrial Filtration.—On a large scale, instead of filter paper, cloth or canvas is generally used and the liquid is squeezed out of the filtering material under pressure in a **Filter Press** (fig. 7).

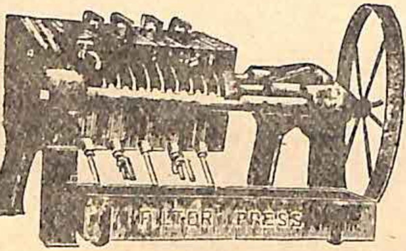

Fig. 7—Filter Press

Soluble Substances—We take a lump of sugar in a tumbler, pour water over it, and allow the liquid to stand undisturbed. We find that, after some time, the lump of sugar disappears under water and water in the tumbler tastes sweet,—most at the bottom and least at the top (we have got *heterogeneous* mixture of water and sugar). We now stir the liquid or pour it from one tumbler to another, when it tastes equally sweet in all its parts (it now becomes *homogeneous*). We have thus prepared a solution of sugar in water ; and unlike the sample of muddy water, we cannot take sugar out of the solution by sedimentation, decantation, filtration etc. We can, however, do it by evaporation, distillation etc.

Again, here we have got the *solution* of a solid (*viz.* sugar) in a liquid (*viz.* water). And though this kind of solution is rather common, we must not forget that we can have other types of solution as well. For example, we have the solution of a gas in water, as in the case of **soda-water**, which is a solution of **carbon dioxide** gas in **water**; or the solution of a liquid in water, as in the case of solution of **bromine** in water. In all the above examples, water is called the **solvent**, and sugar, carbon dioxide or bromine, the **solute**. Thus we see:

solution=solvent+solute

Other solvents.—Water, however, is not the only solvent known. It happens to be one of the most common solvents. Alcohol, petrol, benzene, turpentine, carbon disulphide are examples of other common liquid solvents.

A solution is a homogeneous mixture of two or more substances such that their relative amounts may be gradually changed within certain limits.

N. B.—In the case of a chemical compound, the relative amounts of the constituents *cannot be changed at all.*

Dilute and Concentrated solutions.—The *concentration* of a solution is determined by the amount of solute present in a definite weight of the solvent at a particular temperature (see solubility). If only a small amount of the solute is present, the solution is *dilute*. If the solution contains relatively large amount of the solute, it is *concentrated*,

Saturated Solution

Let us take a little nitre and stir it with water taken in a beaker at the temperature of the laboratory. Nitre dissolves in water. We add a little more. It also dissolves. If we, in this way, go on adding nitre, we shall see that ultimately a point will be arrived at when the solution will *refuse* to take in more nitre; and nitre, *now* added, will remain undissolved. It is clear, therefore, that there is a limit to the power of dissolving nitre by a *definite amount* of water at a *definite temperature*. When the said limit is reached, the solution, we get, is called a *saturated solution at that temperature.*

Thus a solution may *ordinarily* be said to be saturated at a particular temp. with respect to the solute when it cannot dissolve any more of the solute at the temp.; and the solution and the solute are in a state of equilibrium.

Now this state of saturation or equilibrium can be disturbed by raising the temperature of the solution. For example, if the saturated solution of nitre in water, above referred to, be heated, it will be found that the solution can now dissolve more nitre. It will be found further that larger and larger amounts of nitre will be required to make the solution saturated at higher and higher temperatures. When the hot saturated solution is cooled to room temperature, the excess solute is thrown out.

It is sometimes found, however, that the hot saturated solution of some substances like sodium thiosulphate can be cooled slowly to room temperature in the absence of undissolved particles without causing any separation of the excess solute. In that case, the solution contains more solute than it can ordinarily hold to form a saturated solution at the room temperature. Such a solution is called a *supersaturated solution*. But if a fragment of the solute is introduced the excess of the solute is thrown down.

Saturated, Unsaturated and Supersaturated Solutions.—A solution is said to be *saturated* in respect of a solute at a particular temperature when its concentration remains unchanged in contact with the solute at that temperature. If the concentration increases in contact with the solute, it is *unsaturated* ; while if the concentration falls in contact with the solute, it is *supersaturated.*

Solubility.—**The weight in grams of a substance** (*i.e.*, **solute) which when dissolved in 100 grams of a solvent forms a saturated solution at a particular temperature, is called the solubility of the substance (solute) at that temperature.**

Hence, $Solubility = 100 \times \frac{\text{wt. (in gms.) of } solute}{\text{wt. (in gms.) of } solvent}$.

Let m gms. of a solid be present in M gms. of its saturated solution at t°. Then taking x as the solubility of the solid at t°, we find that

$$x = \frac{100m}{M-m}.$$

Determination of the solubility of a substance at room temperature and at temperatures lower or higher than the temperature of the laboratory.

Prepare a cold saturated solution of nitre in a beaker. Heat the beaker, and go on adding nitre to the sol., stirring at the same time, till the temperature rises to 100°. Add some more nitre and stir until some of it is left undissolved. It is a saturated solution at 100°. Now remove the flame. The temperature falls. As soon as the temperature reaches 90°, quickly draw off 10 c.c. of the solution and transfer it to a previously weighed evaporating dish. Call it sol. No. 1 and set it aside. Allow the main solution to cool. When the temperature reaches 80° draw off another 10 c.c. of this solution and pour it into another previously weighed dish and call it sol. No. 2. As the solution of nitre cools down, go on transferring 10 c.c. of the solution at 70°, 60°. 50°, 40°. and 20° and at room temp. in previously weighed basins and call them solution Nos. 3, 4, 5, 6, 7 and 8 respectively.

Take the dish containing sol. No. 1 and weigh it. Heat it on a water-bath to evaporate the liquid carefully till the residue is perfectly dry. Cool it in a desiccator and weigh again. Repeat the processes of heating, cooling and weighing till the final wt. is constant. From the results calculate the solubility of nitre at 90°. And by weighing the other dishes and evaporating the solutions to dryness, cooling and weighing them again, the solubility of nitre can be calculated at different temperatures, *viz*. 80°, 70°, 60°, 50°, 40°. 20°, room temp. etc. Similarly, at *low* temperatures.

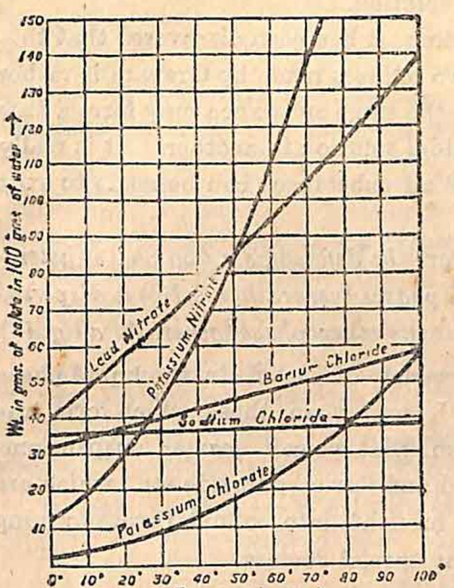

Fig. 8—Solubility Curves.

Solubility Curves.—The solubility of a substance at different temperatures is graphically represented by means of a curve. The curve is called the *solubility curve.*

Influence of Temperature on the Solubility of Solids.—A look at the solubility curve of potassium nitrate (fig. 8) shows that its solubility rises *rapidly* with the rise of temperature. This is almost the general rule. The solubility curve of sodium chloride shows that its solubility rises *very slowly* with the rise of temp.

It is *almost* constant. Hence the curve is *nearly* parallel to the temperature axis. Though it is a general rule that the solubility of solids rises with the rise of temp., there are solid salts whose solubility *falls* with the rise of temperature *i.e.*, they are more soluble in cold water than in hot water. Calcium hydroxide, calcium citrate etc. are examples in point. Again, sometimes *breaks* appear in the solubility curves of some solids. These indicate change in the composition of the solids.

Utility of Solubility Curves—(*What information can be obtained from solubility curves ?*)—The solubility curves enable us—(1) to read out directly the solubility of a substance at a particular temperature ; (2) to get a clear idea of the change in the solubility of substances with change of temperature ; (3) to compare the solubilities of two or more substances at the same temperature ; and (4) to make out which substances will be deposited first when a mixed solution is either evaporated or cooled.

True solution and colloidal solution :

Aqueous solution of substances such as sodium chloride, hydrochloric acid, urea, sugar etc., can readily pass through animal and vegetable membranes such as parchment. Such solutions are called *true solutions.* There are other substances such as gum, glue, starch, albumen, etc. generally of high molecular weights which in aqueous solution fail to do so. Graham called the former class of substances *crystalloid* to distinguish them from the latter class which he named *colloids.* When the colloids are dispersed in some liquid medium such as water, they form *colloidal solution.*

As a result of later investigations, it has been discovered that this rigid distinction between the two classes made by Graham is rather arbitrary, for it was found that the same substance may form a true solution in one medium and colloidal solution in another. It is really a different state of matter in which all substances can be made to exist under suitable conditions.

Colloidal solution may, therefore, be defined as a two phase (heterogeneous) system in which one of the phases (generally a solid) is dispersed in a fine state of division throughout the other phase (generally a liquid).

In colloidal solution, the particles dispersed in the liquid phase are of bigger size (10^{-5} to 10^{-7} cm.) than those which form true solution. Still larger particles form what we call *coarser* suspensions. Substances such as sulphur, gold and ferric hydroxide etc., which are insoluble in water can be also brought into colloidal state forming apparently homogeneous solution by special devices.

Properties of a colloidal solution :

A colloidal solution has a colour often different from the substance in bulk. Thus colloidal solution of gold (gold sol. as it is called) is blue or red according to the size of the colloidal particles.

Colloidal particles can be seen as bright specks of light under a microscope if a strong beam of light is made to pass through the colloidal solution at right angle to the line of view. This phenomenon is known as *Tyndal effect.*

The colloidal particles are found to execute ceaseless zigzag movements, now going up, now going down, stopping and starting again in all directions in a most erratic manner. This phenomenon is known as *Brownian movement.*

The substances in colloidal solution can be precipitated by the addition of electrolytes. This is known as the *coagulation* of colloids.

Application of colloids.—Colloidal sulphur, gold and calcium are used as medicine. Many of the substances used in tanning, dyeing, and in paint and photographic industries are of colloidal nature. Hence the study of colloids is considered important.

Dialysis.—A substance in true solution can be separated from one in colloidal solution by means of a vegetable or animal membrane (parchment, collodin or cellulose). The process of such separation is known as *Dialysis.*

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Dialysis : Expt.—Take a mixture of common salt (*crystalloid*) and gum (*Colloid*) and dissolve it in water. Now place the solution in a shallow bell-jar, the bottom of which is closed by a piece of parchment paper, and suspend it, partly immersed in water, in another jar (fig. 9). After sometime common salt is found to pass readily out of the parchment paper but not the gum. Add $AgNO_3$ sol. to the water in the other jar. A copious *white curdy ppt.* of *AgCl* shows the presence of common salt in the water.

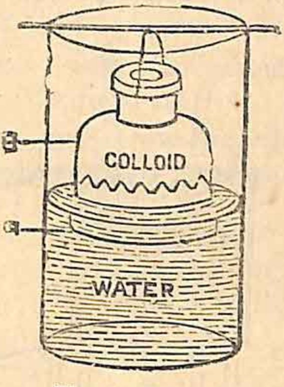
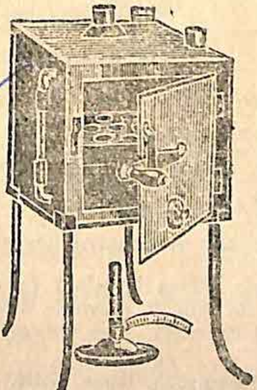


Fig. 9—Dialysis

Desiccation or Drying

Desiccation or Drying. *is the process of removing moisture from substances.* It is effected—(1) by heating the substances (*a*) in a steam-oven at a temp. up to 100° : or (*b*) in an air-oven at a temp. above 100° : or (2) by placing it in a desiccator (ordinary or vacuum) at the ordinary temperature.

Drying at Steam-heat : Steam-oven.—It is a double-cased copper box fitted with a door and a stand at the bottom. The box is heated from below by means of a Bunsen flame (fig. 10). Before heating, the jacket of the steam-oven is filled with water up to about $\frac{1}{3}$rd. of its height. When the water boils, the upper part of the hollow casing becomes filled with steam and the temperature of the interior of the oven approaches 100°. The hollow casing is provided with an opening at the top for the escape of steam. There is a horizontal shelf inside the oven, also made of copper, upon which the substances to be dried are placed.



Fip. 10—Steam oven

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Substances which can be freed from moisture *below* 100° and are decomposed *above* 100°, are usually dried in the steam-oven.

Drying above Steam-heat : Air-oven.—It is a copper box provided with a door and a stand at the bottom. The oven is heated from below by means of a Bunsen flame. There is a horizontal shelf, also made of copper, on which the substances to be dried are placed.

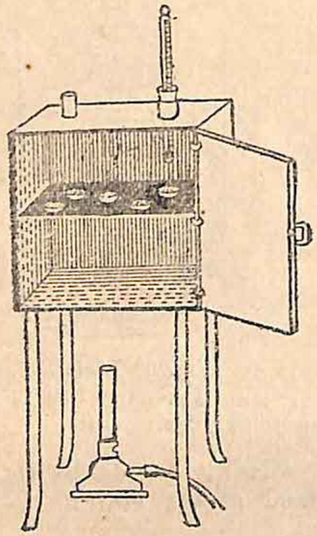


Fig. 11—Air-oven

The temperature of the interior of the oven is noted by introducing a thermometer through a hole at the top of the oven (fig. 11).

An air-oven is used when a substance has to be dried above 100°.

Drying at the ordinary temp. : Desiccator.—The desiccator is a thick-walled glass vessel, contracted in the middle and is provided with a heavy glass lid at the top. Inside the desiccator, at the bottom, is placed the desiccating material which is usually conc. sulphuric acid or *anhydrous* calcium chloride. A perforated circular disk, made of zinc or porcelain, is placed upon the portion of the apparatus projecting inside. Substances, to be dried, are placed on the disk. The rim of the lid is greased with lard or vaseline so that the lid fits to the body of the desiccator perfectly *air-tight*.

N. B.—(1) The desiccator serves **two-fold** functions :—(*a*) it desiccates the substances placed inside ; and (*b*) it prevents them from coming in contact with the atmospheric moisture.

(2) Substances which decompose when dried by heat, are usually dried by being placed in an *ordinary* desiccator at the atmospheric temperature and pressure ; or *sometimes* in vacuo in a *vacuum desiccator* (fig. 12).

(3) Desiccators are also used in chemical analysis for cooling *crucibles etc.* after heating and before they are weighed.

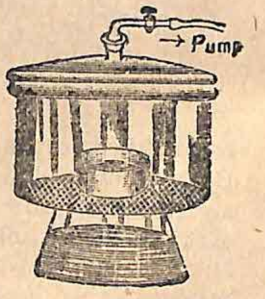


Fig. 12—Vacuum desiccator

Distillation.—*Distillation consists in converting a liquid* (either by the application of heat, or by the reduction of pressure, or by both) *first* into *vapour* and then *condensing the vapour into the same liquid*, which trickles down *in another cold vessel.* Now conversion of a liquid into its vapour is *vaporization* ; and condensation is the process of converting vapours into liquids by the application of cold. *Distillation*, therefore, involves *two* operations : **vaporization** and subsequent **condensation.**

Expt.—Take the liquid, to be distilled, in a distilling flask. Introduce the side-tube of the distilling flask through a cork into a Liebig's condenser (fig. 13). It consists of a narrow glass tube jacketed by a wide glass tube having two side-tubes (or branch-tubes) *near* the ends. Cold water enters the jacket by the lower side-tube and after circulating round the narrow tube and getting heated, leaves by the upper side-tube. Put a clean flask (called *receiver*) at other end of the condenser. Now introduce a thermometer into the distilling flask through a cork fitted to its neck. Place the bulb of the thermometer slightly below, and nearly opposite, to the side-tube. Heat the distilling flask over a piece of wire-gauze by means of a Bunsen flame, till the liquid in the flask boils. The vapour of the liquid, giv n off during boiling, passes through the Liebig's condenser and due to the cooling action produced by the circulation of cold water through the jacket, is condensed back into the liquid, which trickles down and collects inside the receiver. The liquid collected in the receiver, is called the **distillate.**

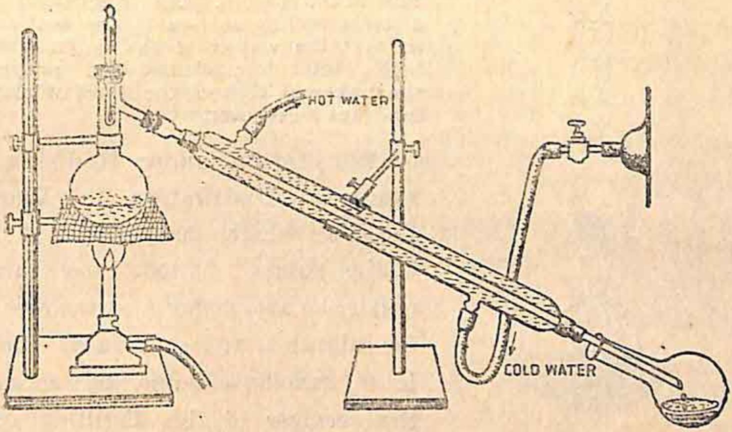


Fig. 13—Distilling apparatus ; distillation

By the process of distillation, we can purify a liquid from its non-volatile dissolved impurities. A solid may also be recovered from its solution by distilling off the solvent.

A mixture of two liquids differing in their boiling points may be separated by fractional distillation.

Expt.—Take a mixture of ether (b.-p., 35°) and aniline (b.-p., 182°) in a distilling flask connected with a Liebig's condenser and a reciever. Heat the flask carefully. When the temperature rises to 35°, ether distils over and collects in the receiver cooled in ice. Change the receiver and heat the flask again. When the temp. rises to 182°, aniline distils over and collects in the second receiver. Thus the two liquids are separated by fractional distillation; and ether is obtained as the **1st fraction** while aniline is obtained as the **2nd fraction.**

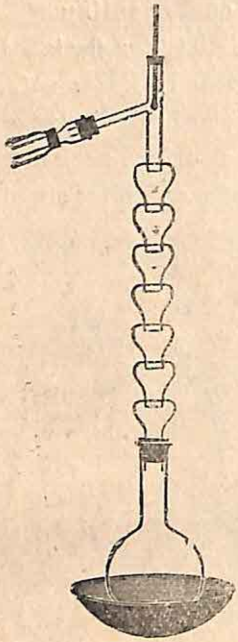


Fig. 14—Fractionating column

N. B.—Ether is a highly inflammable liquid.

Fractionating Column.—Fractionation of a mixture of liquids is more effectively carried out by attaching a fractionating column (fig. 14) to the mouth of the flask, and a Liebig's condenser fitted to the side-tube of the column. The object is to present a large cooling surface to the hot vapours, so that the vapour of the liquid of higher boiling-point is condensed and returned to the flask and that of the liquid of lower boiling-point passes over.

Distillation under Reduced Pressure or Distillation in Vacuo.—Liquids which decompose at their boiling-points cannot be distilled under the atmospheric pressure. They are distilled under reduced pressure. It is usually effected by connecting the receiver of the distilling apparatus with a filter-pump to exhaust the air out with a view to reducing the pressure inside and producing partial vacuum (fig. 15). The process is known as distillation under reduced pressure or, less accurately, distillation in vacuo.

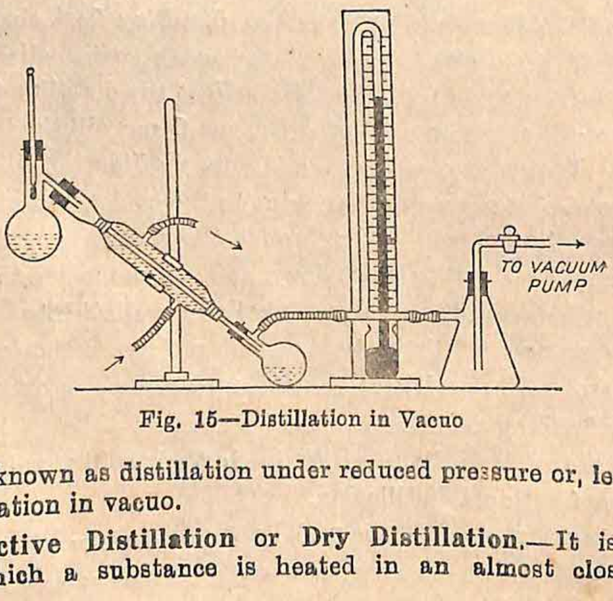


Fig. 15—Distillation in Vacuo

Destructive Distillation or Dry Distillation.—It is the process in which a substance is heated in an almost closed vessel, like a retort, and the volatile products, given off by the decomposition of the substance, are condensed and collected in other vessels.

Example—The destructive distillation of coal is carried out by heating it in retorts and collecting the volatile products given off (*viz.* coal tar, ammoniacal liquor, etc.) by condensation in other vessels.

Sublimation.—There are some solids like camphor, iodine, napthalene etc. which directly pass into the vapour state from solid by application of heat and the reverse change takes place on cooling. The substance does not pass through the intermediate liquid state. These solids are said to *sublime.*

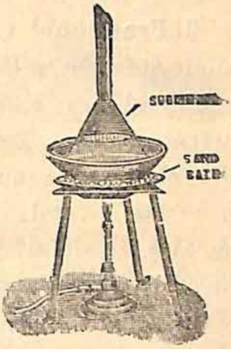


Fig. 16—Sublimation

Experiment.—Take iodine in a porcelain basin and cover it with an inverted funnel (fig. 16). Close the end of the funnel with glass wool and heat the basin on a sand-bath. Iodine sublimes off and collects inside the funnel in a beautiful crystalline form. Also try with camphor, salammoniac and calomel.

Def.—*Sublimation is the process of converting a solid directly into its vapour and condensing the vapour back into the solid state having the same composition.* (—*Mellor.*)

The product of sublimation is called the **Sublimate.**

Separation of mixture of pure sand and salammoniac by sublimation.—Take the mixture in a porcelain basin. Place it on a tripod stand fitted with wire-gauze. Cover the basin with another porcelain basin. Cool the upper basin by placing a piece of *wet* blotting-paper on it, and heat the lower basin for a pretty long time (fig. 16). Now stop heating. Cool and separate the two basins. Sal ammoniac is found to have collected inside the upper basin as a sublimate, while sand is left in the lower basin.

Crystallization : Crystals.—When the solution of a solid in a liquid, saturated at a higher temperature, is allowed to cool down, it is usually found that a quantity of the solid, held in solution, is deposited *spontaneously* in the form of particles having regular and definite geometric shape. These particles are called crystals, and the process is known as *crystallization.*

What are Crystals ?—**Crystals are homogeneous solids, bounded by plane faces, meeting in sharp edges and having regular and definite geometric shape, which shape they spontaneously acquire during their formation.**

Every solid has its own crystalline form. A crystal of common salt is cubic, while alum crystal is like a double pyramid, When a perfect crystal is broken, it breaks into smaller cyrstals each of which is an exact replica of the larger one.

Solids possessing no crystalline shape are called *amorphous* solids. *Examples.*—Glass, pitch, lime, etc.

Purification of solids by Crystallization.

1 **Recrystallization**.—When a crystalline solid contains a very small quantity of an insoluble substance, or a soluble substance having a sufficiently divergent solubility from it, make a saturated solution of the solid in water at a higher temp., filter *rapidly*, and allow the filtrate to cool. We get crystals of the pure solid. Repeat the process if necessary.

2. **Fractional Crystallization.**—A mixture of two or more soluble solids differing in their solubilities may be separated by the process of fractional crystallization. Take a mixture of potassium nitrate and copper nitrate. The latter is more soluble than the former. Dissolve the mixture in the minimum quantity of hot water. On cooling, colourless crystals of potassium nitrate separate out and copper nitrate remains in solution. Crystals of potassium nitrate are filtered off, washed with water till free of copper nitrate and then dried. On evaporating the filtrate, we get crystals of copper nitrate.

Water of Crystallization.—Many solids while crystallizing out of **aqueous** solution, yield crystals containing **combined** water, taken up from the solution. Each molecule of the crystalline substance is found to be in *combination* with a definite number of molecules of water. The compound, so formed, has to depend, for its particular crystalline shape, upon these molecules of water. When the water is taken away, the particular crystalline shape is lost. Water so associated with crystals as an essential part of their constitution is known as *water of crystallization*. The substance is called the *crystallo-hydrate*, or simply **hydrate** (—*Taylor*).

Examples :—Oxalic acid, $H_2C_2O_4$, $2H_2O$; *blue vitriol*, $CuSO_4$, $5H_2O$; *green vitriol*, $FeSO_4$, $7H_2O$, etc.

Action of heat on salts containing Water of Crystallization.—Though the effect of heat on crystals of different salts, containing water of crystallization, is not identical, still all of them lose water on heating. The definite crystalline shape disappears. The dry solid left, after heating, is called the **anhydrous** or **dehydrated** (*i.e.*, without water of crystallization) salt.

In some cases this loss of water is attended with change of colour. Thus hydrated copper sulphate is **blue** in colour ; but when made anhydrous by heat, it becomes **white** in colour.

Water is not an essential part of all crystals.—It must be clearly understood that all crystalline solids do not necessarily contain water of crystallization. We may have substances which are crystalline in shape but which do not contain water of crystallization under ordinary circumstances. Common salt, nitre, potassium chlorate, silver nitrate, etc. are the best examples.

Determination of the water of Crystallization of blue vitriol.—Expt.—Take a pair of clock-glasses, held together by a clip and weigh it carefully (fig. 17). Place some powdered crystals of *dry* and *pure* blue vitriol in the lower clock-glass, cover it with the upper clock-glass, and weigh the whole over again. Now make a passage for the escape of water of crystallization as steam by sliding the upper clock-glass a little, and place the pair of clock-glasses with blue vitriol in an air-oven (fig. 11). Heat the air-oven by means of a Bunsen flame so as to raise the temperature of the oven first to 100° and then very carefully to about 230°. After about three quarters of an hour, the salt becomes *anhydrous* and *white* in colour. Slide the upper clock-glass back to its former position, take the clock-glasses (with the contents) out, cool them in a desiccator, and weigh. To ensure complete removal of water of crystallization, repeat the processes of heating, cooling and weighing till the *final weight is constant.*

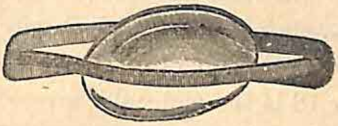


Fig. 17—Clock-glasses with clip.

N.B.—As blue vitriol decomposes at 300°, it is *carefully* heated in an *air-oven* and not in a naked flame.

Calculation.—Let the wt. of clock-glasses + clip $= w_1$ gms.

Wt. of clock-glasses + clip + blue vitriol $= w_2$ gms.

Wt. of clock-glasses + clip + anhydrous $CuSO_4 = w_3$ gms.

$\therefore$ wt. of blue vitriol taken $= (w_2 - w_1)$ gms.

and wt. of water of crystallization $= (w_2 - w_3)$ gms.

Now, $(w_2 - w_1)$ gms. of blue vitriol contain $(w_2 - w_3)$ gms. of water of crystallization.

$\therefore$ 100 gms. of blue vitriol will contain

$$(w_2 - w_1) : 100 :: (w_2 - w_3) : x$$

Or, $x = \dfrac{100 \times (w_2 - w_3)}{(w_2 - w_3)}$ = percentage of water of crystallization.

Deduction of the formula of blue vitriol.—Let the *formula* of blue vitriol be $CuSO_4, nH_2O$. We want to prove that $n=5$.

From the above data we see that the wt. of *anhydrous* copper sulphate is $(w_3 - w_1)$ gms ; and $(w_3 - w_1)$ gms. of *anhydrous* $CuSO_4$ combine with $(w_2 - w_3)$ gms. of water of crystallization. Therefore, 159·5 gms. *i.e.* the *gm.-mol. wt.* of $CuSO_4$ will combine with

$$(w_3 - w_1) : 159{\cdot}5 :: (w_2 - w_3) : x$$

$$\text{Or,}\ x = \frac{159{\cdot}5 \times (w_2 - w_3)}{(w_3 - w_1)}.$$

If the experiment be carefully performed and the values of w_1, w_2, w_3, etc be substituted, it will be found that $x = 90$. Now, 159·5 stands for 1 molecule of $CuSO_4$ while 90 can stand for 5 molecules of water, for 18 is the molecular wt. of water. Hence $n = 5$ and the formula of blue vitriol is $CuSO_4, 5H_2O$.

Separation of the Components of some common Mixtures of Solids

(*a*) *Separation of the components of gun powder.*

It is a mechanical mixture of charcoal, sulphur and nitre. Treat gunpowder with carbon disulphide in a beaker and stir it by means of a stirring rod till sulphur completely dissolves in carbon disulphide.

Filter

Filtrate
It is a solution of sulphur in carbon disulphide. Evaporate it. We get **sulphur**,

Residue
Boil the residue with water till nitre completely dissolves.
Filter

Filtrate
Sol. of nitre in water. Evaporate the filtrate to *dryness*. We get **nitre**.

Residue
Charcoal left on filter-paper. Wash and dry it.

(*b*) *Separation of a mixture of sulphur, nitre and sand.*

Treat the mixture with carbon disulphide in a beaker and stir till sulphur dissolves completely.

Filter

Filtrate
It is a solution of sulphur in carbon disulphide. Evaporate the solution when we get **sulphur**.

Residue
It is a mixture of nitre and sand. Boil the residue with water till nitre is completely dissolved.
Filter

Filtrate
Sol. of nitre in water. Evaporate the filtrate. We get **nitre**.

Residue
Sand left is washed with water and dried.

(c) *Separation of the components of a mixture containing iodine, common salt and powdered glass.*

Take the mixture in a retort the end of which has been put inside a flask kept cooled by water. Heat the retort carefully, when iodine sublimes off and collects in the receiver.

Heated

Sublimate

Iodine

Residue

It is a mixture of common salt and glass. Boil it with water till salt completely dissolves. Filter

Filtrate

It is a solution of common salt in water. Evaporate it to dryness. We get **common salt.**

Residue

Powdered glass.

Wash and dry it.

Exercise

1. What methods other than extraction by solvent will you use to separate (i) intimate mixture of finely powdered *Iron ore* and *Copper ore*, (ii) mixture of *sand* and *Iodine*, (iii) mixture of dry powdered *Nitre* and dry *powder of Sulphur*, (iv) mixture of *sand* and *Lead-shavings* ? *Pat. 1937.*

2. You are given a mixture of sand, chalk and common salt. How will you find out the percentage of the three constituents ? *C. U., 1910.*

3. How does a mechanical mixture differ from a chemical compound ? Is gunpowder a chemical compound ? How would you separate the constituents of *gunpowder* and *brine* ? *Comb., S. C., 1927 ; All 1912 ; C. U., 1917 '33, '36, '38, '40. Cal. Pre-U. 1961*

4. Write short notes on :

   (a) Water of Crystallisation and Sublimation. *Cal. Pre-U, 1961*

   (b) Destructive Distillation. *Cal. Pre-U. 1966*

5. You are given a mixture of Iron-filings, calomel, sulphur, sugar and powdered glass. State how you will separate the ingredients and obtain them in the pure state. *Pat., 1917 ; C. U., 1915*

6. A salt deposit is found to consist of a mixture of sodium carbonate, sodium sulphate and sand. How will you find the proportions of these substances, and how will you separate them ?

7. Explain and illustrate with examples :

   True Solution and Colloidal Solution.

Cal. Pre-U. 1967

CHAPTER V

SYMBOL, FORMULA, VALENCY AND EQUATION

Symbol.—A *symbol* is an abbreviation for the full name of an element.

The abbreviations of elements now used were suggested by Berzelius in 1811.

Generally the initial letter of the name of an element in capital is used to represent it *e.g.*, **hydrogen** is represented by **H; oxygen** by **O; carbon** by **C; nitrogen** by **N;** etc.

When the names of two or more elements commence with the same letter, the initial letter and another letter which is prominently heard in pronouncing the word are used ; one of the elements may, however, be represented by the initial letter only. For example, the names of the four elements **barium, boron, bismuth** and **bromine** commence with b : they are represented respectively by the symbols **Ba, B, Bi, and Br.** Some chemical symbols are derived from Latin names of the elements they represent ; thus **copper** is represented by **Cu** (Lat., *cuprum*), **iron** by **Fe** (Lat, *ferrum*), **sodium** by **Na** (Lat. *natrum*), **gold** by **Au** (Lat., *aurum*), **silver** by **Ag** (Lat., *argentum*), **mercury** by **Hg** (Lat., *hydrargyrum*), etc.

Significance of a symbol.—A symbol is not only the shortened name of an element but it also denotes one atom of the element and a quantity *proportional* to the atomic weight of the element. It has got both a *qualitative* and *quantitative* significance. Thus—

C represents one **atom of carbon** and
12 parts by wt. of carbon.

O represents one **atom of oxygen** and
16 parts by wt. of oxygen.

When the molecule of an element consists of more than one atom, the fact is expressed in chemical notation by placing small numerals immediately after the symbol of the element. Thus H_2 represents a molecule of hydrogen consisting of two atoms ; O_2—a molecule of oxygen consisting of two atoms, O_3—a molecule of ozone consisting of three atoms of oxygen ; and so on. But 2H stands for 2 atoms of Hydrogen *not united* together.

The following is a list of important elements with their symbols.

Non-metals

Solid

Name	Symbol	At. wt.
Boron	B	11
Carbon	C	12
Silicon	Si	28·06
Phosphorus	P	31
Sulphur	S	32

Liquid

Name	Symbol	At. wt.
Bromine	Br	80

Gaseous

Name	Symbol	At. wt.
Hydrogen	H	1·008
Nitrogen	N	14
Oxygen	O	16
Fluorine	F	19
Chlorine	Cl	35·46

Solid

Name	Symbol	At. wt.
Iodine	I	127

Metals.

Arranged as in the Electro-chemical Series (—*Mellor*)

Name	*Symbol*	*At. wt.*	*Mt. point*	*Sp. gr.*
Potassium	K	39·1	62°	0·86
Sodium	Na	23	98°	0·79
Calcium	Ca	40	800°	1·52
Magnesium	Mg	24·3	651°	1·75
Aluminium	Al	26·97	658°	2·7
Chromium	Cr	52	1530°	6·74
Manganese	Mn	55	1240°	8·0
Zinc	Zn	65·3	419°	6·9
Cadmium	Cd	112·4	321°	8·6
Iron	Fe	55·84	1533°	7·8
Cobalt	Co	58·9	1530°	8·8
Nickel	Ni	58·69	1482°	8·9
Tin	Sn	119	232°	7·22
Lead	Pb	207·2	327°	11·3
Antimony	Sb	121·76	630°	6·7
Bismuth	Bi	209	271°	9·8
Arsenic	As	75	×°	5·73
Copper	Cu	63·5	1803°	8·95
Mercury (*liquid*)	Hg	200·6	−39°	13·6
Silver	Ag	107·8	960·5°	10·5
Palladium	Pd	106·7	1550°	11·4
Platinum	Pt	195·2	1755°	21·4
Gold	Au	197·2	1065°	19·3

Formula or Molecular Formula—**It is the symbolic representation of the molecule of a substance.**

Thus the formula of hydrogen is H_2, that of phosphorus is P_4. In the case of a compound, the formula is built up by writing, side by side, symbols of its constituent elements, the number of atoms of each element present in a molecule being indicated by numerals. Thus a molecule consisting of one atom of sodium (symbol, Na) and one atom of chlorine (symbol, Cl) is represented by the united symbols, NaCl ; a molecule of ammonia consisting of one atome of nitrogen and three atoms of hydrogen is likewise represented by the formula NH_3.

It must, however. be clearly understood that H_2O does not stand for water. It stands for one molecule of water. When we drink water it would not be quite correct to say that we drink H_2O, for we do not drink only one molecule of water.

In order to express 2, 3, or x **molecules** of a substance, we place a numeral before its formula *e g.*, $2H_2O$, $3H_2O$, xH_2O, to mean two, three, or x molecules of water respectively.

Significance of a Formula.—Like the symbols, the formulae have a *qualitative* as well as a *quantitative* meaning. The formula of a compound tells us—(1) what elements the compound contains ; (2) how many atoms of each element are present in one molecule of the compound ; (3) how the atoms in the molecule are arranged (—*Structural formula*) ; (4) the weight of the compound proportional to its molecular weight , and (5) the relative wts. of the elements present in the molecular wt of the compound.

Valency.

We have seen that the molecule of a compound is formed by the union of two or more atoms which are bound together by *Chemical force.* This union between the atoms does not take place in a haphazard manner, but it follows a definite rule. Thus any *one* atom of *bromine* is found *always* to combine with *one* atom of hydrogen giving a molecule of the compound of hydrogen and bromine. Similarly, any *one* atom of calcium *always* combines with *two* atoms of hydrogen giving a molecule of the compound of calcium and hydrogen. Such is also the case with other elements and hydrogen.

It is clear, therefore, that atoms of different elements combine with one or more atoms of hydrogen, for they have an ability to do so, and their *combining capacity* or *valency*, as this ability is called, is not the same.

Now, it may appear strange that we have always been comparing the combining capacities of different elements with that of hydrogen. The reason is that as no compound of hydrogen is known (except hydrozoic acid, N_3H) which contains more than one atom of an element combined with one atom of hydrogen, chemists have taken an atom of hydrogen as the *standard* for measuring the valencies of the atoms of different elements.

Again, when we consider the cases of (i) hydrochloric acid (HCl), (ii) water (H_2O), (iii) ammonia (NH_3) and (iv) methane gas (CH_4), we find that in a molecule of the—

1st compound, 1 atom of chlorine combines with 1 atom of hydrogen
2nd compound, 1 atom of oxygen combines with 2 atoms of hydrogen.
3rd compound, 1 atom of nitrogen combines with 3 atoms of hydrogen.
4th compound, 1 atom of carbon combines with 4 atoms of hydrogen.

It shows that atoms of different elements possess different capacities for combining with hydrogen. Oxygen, for example, possesses twice the combining power of chlorine, for it can hold in chemical union twice as many hydrogen atoms. Similarly, nitrogen and carbon atoms possess respectively three and four times the combining power of chlorine. With a little thought it will also become apparent that hydrogen and chlorine have the same combining power since 1 atom of the one combines with 1 atom of the other. And as the valency of hydrogen atom is taken to be equal to 1, the valency of chlorine becomes 1, that of oxygen 2, that of nitrogen 3, and that of carbon 4. Some elements, however, are found not to combine with hydrogen at all, but they do so with other elements like chlorine, fluorine, etc. We have seen that chlorine is monovalent. We can, therefore, measure the valencies of these atoms *indirectly* by determining how many atoms of chlorine wlll combine with one atom of each. Thus gold does not combine with hydrogen directly, but it combines with chlorine in such way that 1 atom of gold is in union with three atoms of chlorine. And as the valency of chlorine is 1, that of gold, on that basis, is 3.

Def. of Valency.—The valency of an element is its capacity for combining with other elements and is measured by the number of hydrogen or chlorine atoms which combine with or are displaced by one atom of the element.

Classification of elements according to their Valencies

Monads	*Diads*	*Triads*	*Tetrads*	*Pentads*	*Hexads*
Hydrogen Fluorine Chlorine Bromine Iodine	Oxygen *Sulphur*	Boron *Nitrogen* *Phosphorus*	Carbon Silicon Sulphur	*Nitrogen* *Phosphorus*	Sulphur
Potassium Sodium *Mercury* (-*ous*) *Copper* (-*ous*) Silver	Calcium Strontium Barium Zinc Magnesium *Copper* (-ic) *Mercury* (-*ic*) *Iron* (-*ous*) *Tin* (-*ous*) *Lead* (-*ous*)	Aluminium *Gold* (-*ic*) Bismuth *Iron* (-*ic*) *Antimony* (-*ous*)	*Tin* (-*ic*) Platinum *Lead*	Arsenic *Antimony* (-*ic*)	

Thus elements like chlorine, bromine, etc., an atom of which can combine with one atom of hydrogon, are called *monovalent elements* or simply, *monads*. Elements like oxygen, calcium, etc. (an atom of which can combine with two atoms of hydrogen or with two atoms of chlorine) are called *divalent elements or diads*. Similarly, we have *trivalent*, *tetravalent*, *pentavalent*, *hexavalent* elements. Then again, though different elements generally possess different valencies, two or more elements may have the *same* valency ; and, as we shall see afterwards, the same elements may have different valencies.

The conception of valency may also be extended to the case of **Compound Radicals or Groups.**

Classification of Radicals according to Valency.

Monovalent	*Divalent*	*Trivalent*	*Tetravalent*
Ammonium (NH_4) Cyanogen (CN) Hydroxyl (OH) NO_2 NO_3	CO_3 SO_3 SO_4	PO_4 PO_3 BO_3 Ferricyanide $Fe(CN)_6$	Ferrocyanide $Fe(CN)_6$

Practical use of the Knowledge of Valency : Writing Chemical Formula.—In addition to the theoretical interest, the classification of the elements according to their valencies is very useful, for it provides us with a means of avoiding mistakes in writing chemical formulae and saves the trouble of learning great number of formulae by heart. The following rule will give a general idea of the subject :—

Rule.—*When two elements A and B combine together to form the compound AB, then the number of atoms of A combining with the number of atoms of B to form a molecule of AB, will be inversely as the valencies of A and B.*

Application of the Rule.—Let us try to write the formula of phosphorus pentachloride. Since phosphorus is *pentavalent* and chlorine *monovalent*, the composition of phosphorus pentachloride will be such that the number of atoms of phosphorus and that of chlorine present in the molecule are inversely as their valencies, that is *as* 1 : 5. Or, the formula is PCl_5. The composition of ferric oxide is Fe_2O_3, for ferric iron is *trivalent* and oxygen is *divalent*.

The rule *also* applies to the case of Groups or Compound Radicals. Thus calcium phosphate will have the formula $Ca_3(PO_4)_2$, for Ca is *divalent* and (PO_4) is *trivalent.* For a similar reason, zinc sulphate is $ZnSO_4$; silver nitrate is $AgNO_3$, and so on.

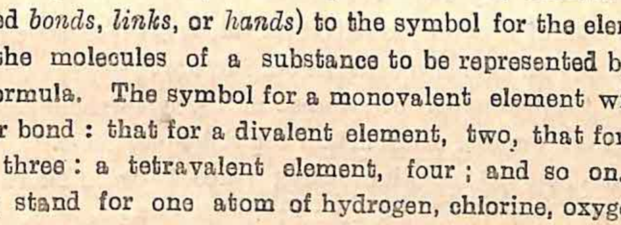
N.B. Elements or radicals do not always exert their maximum valency. This rule, therefore, though useful, may not *alone* lead us to a particular conclusion.

Valency may vary ; Maximum Valency.—The valency of an element is not a constant property. It may sometimes vary , and many elements have *more than one* valency. Thus, nitrogen is trivalent in ammonia, but pentavalent in ammonium chloride, NH_4Cl. Sulphur is divalent in H_2S, tetravalent in SO_2 and hexavalent in SO_3. Phosphorus is a pentad in PCl_5 and triad in PCl_3. It is thus difficult to fix the exact valency of an element. In such cases of variation the rule is to take the *highest number of monovalent atoms, with which one atom of an element is capable of combining, as the valency of the element.* Hence phosphorus is pentavalent, for PCl_5 is the *highest* chloride of phosphorus.

Graphic or Structural Formula.—The valency of an element is sometimes represented by attaching the necessary number of hyphens (also called *bonds, links,* or *hands*) to the symbol for the element. This enables the molecules of a substance to be represented by a kind of graphic formula. The symbol for a monovalent element will have one hyphen or bond : that for a divalent element, two, that for a trivalent element, three : a tetravalent element, four ; and so on. Thus the following stand for one atom of hydrogen, chlorine, oxygen, nitrogen and carbon respectively :—

H – . Cl – , – O – , =N – . =C=

When atoms unite to form molecules, their valency-bonds are joined together. Thus the compounds hydrochloric acid, ammonia, marsh gas, carbon dioxide, ammonium chloride, sulphuric acid, ferric oxide are respectively expressed by the graphical formulae—



Ammonium chloride Sulphuric acid Ferric oxide

Fig. 18—Graphical formula

Chemical Equations.—A Chemical equation represents the final result of the change in composition suffered by a compound, or by two or more elements or compounds when they react with each other to produce that change (*Ramsay*).

In other words—

(i) A chemical equation represents a chemical reaction by means of symbols and formulae with the *sign of equality* or *arrow-heads* in the *middle*.

(ii) It is customary to write down *either* the formula of a substance undergoing the chemical change or the symbols and formulae of the reacting substances (called *reactants*) with the sign of *plus*, as they are before the change, on the left-hand side.

(iii) While the symbols and formulae of the products, also with the sign of *plus*, as they are obtained after the reactions, on the right-hand side.

(iv) The sign of equality or arrow-head between the two sides stands for the word '*to produce*'.

(v) The sign of plus on the left-hand side means '*reacts with*' while that on the right-hand side means '*in addition to*'.

(vi) The total number of atoms on the left-hand side is *always* equal to the total number of atoms on the right-hand side.

Thus the chemical reaction taking place between zinc and *dilute* sulphuric acid is represented by the equation—

$$\underset{\substack{\text{(Reacting substances)}\\ \text{Total no. of atoms is 8}}}{Zn + H_2SO_4} \quad = \quad \underset{\substack{\text{(Products)}\\ \text{Total no. of atoms is 8}}}{ZnSO_4 + H_2}$$

The sign + on the left-hand side signifies that Zn *reacts with* H_2SO_4 ; while the sign + on the right-hand side shows that the product $ZnSO_4$ is obtained *in addition to* the product hydrogen.

The Full Meaning of an Equation. The equation—

$H_2 + Cl_2 = 2HCl$ tells us *qualitatively* that

(1) Hydrogen *reacts chemically* with chlorine to produce hydrogen chloride , and *quantitatively*,

(2) 1 molecule of hydrogen combines with 1 molecule of chlorine to produce 2 molecules of hydrogen chloride ,

(3) 2 parts by wt. of hydrogen combine with 2 × 35·46 parts by wt. of chlorine to give 2 × 36·46 parts by wt. of HCl.

(4) The total wt. of the reacting substances (*viz* 2 + 2 × 35·46) *before the change*, is equal to the total wt. of the products (*viz* 2 × 36·46) *after the change*.

(5) The total number of atoms on the left-hand side, *viz* $2+2$, is equal to the total number of atoms on the right, *viz* $2\times(1+1)$, and here, *only in the case of gases*, it *also* tells us *volumetrically* that,

(6) 1 vol. of hydrogen combines with 1 vol. of chlorine to produce 2 vols. of hydrogen chloride.

Limitations of a Chemical Equation *(What an equation does not show)*.—But an equation *ordinarily does not* tell us—

(1) whether heat is *evolved* or *absorbed during* the chemical reaction ;
(2) the condition under which the chemical reaction takes place ;
(3) the time taken for the completion of the reaction ,
(4) the physical states of the substances concerned ,
(5) the concentration of the reacting substances , and
(6) whether the reaction is reversible or not.

Writing Correct Equation.

(1) Magnesium burns in oxygen giving magnesium oxide. The equation may be $Mg+O=MgO$, but, the smallest quantity of oxygen which occurs in the free condition, is the molecule of oxygen consisting of 2 atoms of oxygen, we must write O_2 and *not* O. We, therefore, multiply the eq. by 2 right through. It becomes $2Mg+O_2=2MgO$. Also we write 2Mg, and not Mg_2, for we do not know how many atoms of magnesium are present in 1 molecule of Mg.

(2) Aluminium reacts with HCl giving off hydrogen and producing aluminium chloride. Now Al, being trivalent, 1 atom of it shall replace 3 atoms of hydrogen from HCl. But 1 molecule of HCl contains 1 atom of hydrogen. Hence we take 3 molecules of HCl and the eq. becomes $Al+3HCl=AlCl_3+3H$. And as the smallest quantity of hydrogen which occurs free is the molecule of hydrogen containing 2 atoms, we multiply the eq. by 2 right through, and get.

$$2Al+6HCl=2AlCl_3+3H_2.$$

(3) *Red-hot* iron decomposes *steam* giving off hydrogen and producing Fe_3O_4. We try to write $Fe+H_2O\rightarrow Fe_3O_4+H_2$. This equation *has not been balanced* and is *wrong*. Now to get Fe_3 we must take 3Fe and to get O_4 we must take $4H_2O$. The equation, therefore, becomes $3Fe+4H_2O=Fe_3O_4+4H_2$. This is correct.

(4) Calcium chloride solution gives a white ppt. of AgCl with silver nitrate sol. $CaCl_2 + 2AgNO_3 = 2AgCl + Ca(NO_3)_2$. It is clear that both Ag and Cl being monovalent, we must take 2 molecules of $AgNO_3$ to have 2 atoms of Ag, to combine with 2 atoms of chlorine present in $CaCl_2$ molecule. Hence the above equation.

Types of Chemical reaction.

(1) **Direct Union or Combination or Synthesis.**—*Synthesis* (*Syn*=with, *tithemi*=I place) means putting together and the process is termed synthesis when a compound is formed by the direct combination of its constituents. When magnesium is burnt in air, the metal directly unites with oxygen of the air giving the compound magnesium oxide.

Hydrogen + Oxygen = Water

$$2H_2 + O_2 = 2H_2O$$

Magnesium + Oxygen = Magnesium oxide (or Magnesia)

$$2Mg + O_2 = 2MgO$$

(2) **Direct Decomposition or Analysis.**—This type is the exact opposite of the *first* type. In this process a compound is broken up into its constituents. 'Analysis' (*Ana*=up, *lyein*=to loosen) means separating or taking apart. Red oxide of mercury, when strongly heated, breaks up into its constituents, *viz* mercury and oxygen.

Oxide of Mercury = Mercury + Oxygen

$$2HgO = 2Hg + O_2$$

(3) **Displacement, Replacement or Substitution.**—In this process one element expels another element from a compound and takes its place. Thus zinc replaces hydrogen from sulphuric acid (*dilute*) when the two are brought in contact with each other.

Zinc + Sulphuric acid = Zinc sulphate + Hydrogen

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

(4) **Double decomposition or Mutual Exchange.** (*Metathesis*).—It is a process in which the constituents of two compounds change places. Strictly speaking, this class of changes involves the first two processes, *viz* decomposition and recombination. Thus when mercuric chloride is treated with potassium iodide in solution in water, we get, by mutual exchange, mercuric iodide and potassium chloride.

Mercuric chloride + Potassium iodide = Potassium chloride + Mercuric iodide

$$HgCl_2 + 2KI = 2KCl + HgI_2$$

(5) **Re-arrangement of atoms or Isomerism.**—In this process by the simple re-arrangement of the atoms present in the molecule of a substance, the molecule of altogether a *new* substance is formed, due to the change of condition. The proportion of each element present is not altered. Thus ammonium cyanate, when heated, gives urea by the simple re-arrangement of atoms.

$$\underset{\text{Ammon. cyanate}}{NH_4(CNO)} = \underset{\text{Urea}}{CO(NH_2)_2}$$

Method of bringing about or inducing a Chemical Action.

The following are the different methods of inducing a chemical action :—

(1) **Simple Contact.**—When two or more substances happen to react together to give a chemical compound, they must necessarily be in actual contact. In fact, contact is the most important condition of chemical action. Crystals of *iodine* may be carefully placed side by side with *phosphorus* without any chemical reaction; but the very moment they are brought in contact with each other, vigorous chemical action takes place and we get iodide of phosphorus.

(2) **Solution.**—Contact between the reacting substances sometimes more *readily* and *closely* brought about by having at least one of them in solution. Dry *sodium bicarbonate* does not react with solid *tartaric acid* when they are *thoroughly* mixed together in a mortar (fig. 19), but the solution of sodium bi-carbonate in water reacts vigorously when treated with tartaric acid.

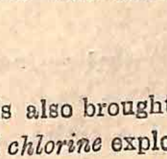


Fig. 19.—Pestle and mortar

(3) **Heat.**—Heat usually expedites chemical action. In some cases the application of heat is absolutely necessary to bring about a chemical action. For example, heat is absolutely required to decompose *mercuric oxide* into mercury and oxygen.

(4) **Light.**—Sometimes chemical action is also brought about in presence of light. A mixture of *hydrogen* and *chlorine* explodes when exposed to light due to the formation of hydrochloric acid gas. No

explosion takes place when the mixture is kept in the dark. Photography depends upon the effect of light on *silver halides.*

(5) **Electricity.**—Electricity plays an important part in bringing about a chemical action. It can decompose a chemical compound into its elements. *Fused sodium chloride* is decomposed into sodium and chlorine by means of electric current. It can also bring about the combination of elements *i.e.*, it can form chemical compounds. *Hydrogen* and *oxygen* combine together when an electric spark is passed through the mixture of the two in *right proportions.*

(6) **Pressure : Percussion.**—Chemical action may sometimes be induced by the influence of pressure. When the two gases *hydrogen chloride* and *phosphuretted hydrogen* are subjected to increased pressure, they combine together to give the solid phosphonium chloride. In the case of ordinary crackers (*bhui patka*) made with *chlorate of potash* and *arsenic sulphide* or *sulphur*, we have got the example of a chemical action brought about by pressure. Similarly, a match stick can be inflamed by rubbing its head against the match box or any other rough surface.

(7) **Sound** (*vibration*).—*Acetylene* is decomposed into carbon and hydrogen by the loud *sound* produced when *mercury fulminate* is exploded near the gas.

(8) **Catalytic agent.**—There are also certain reactions which are able to proceed readily in the presence of (*i.e.*, in contact with) very small quantities of a third substance which itself remains unchanged in mass and in composition at the conclusion of the action. The substance is called a *catalyst*, and the phenomenon is known as *Catalysis* (*Cata*=down, *lyein*=to loosen).

Illustration :—Sulphur dioxide combines with oxygen to form sulphur trioxide. This oxidation of sulphur dioxide takes place very energetically in contact with finely divided, moderately heated platinum which, however, remains unchanged at the end of the reaction. Platinum here acts as a catalytic agent.

Tests of Chemical Action

A chemical action must satisfy the following tests :

(i) there *must be* either *absorption* or *evolution of heat.*

(ii) The action *shall* take place between *fixed quantities* of the reacting substances.

Exercise.

1. Give a full account of what you know about valency. *C. U. 1957.*

2. What do you understand by monovalent and trivalent elements? Give examples.

3. Explain what is meant by the valency of—(1) phosphorus, (2) copper, (3) sulphur, (4) nitrogen. How may the valency of one and the same element vary?

4. What do you understand by the valency of elements? How is it measured? Arrange the following elements according to the valency :—carbon, nitrogen, chlorine, calcium, mercury. Give graphic formula of one compound of each in which the valency is fully satisfied. *Mad., 1931 ; C. U. 1916.*

5. Explain fully what the formulae O_2 and CO_2 represent.

6. State all that is implied by the chemical equation ; $2H_2+O_2=2H_2O$.

J. Cam., 1924 ; C. U. 1930 ; Nag., 1932.

7. What is meant by chemical equation? What is its limitation? Show clearly giving suitable examples the information conveyed by an equation. Give the *full meaning of* :—$Mg+H_2SO_4=MgSO_4+H_2$.

C. U. 1939 ; Punj., 1929 ; Delhi, 1948.

8. Explain the term "catalysis" with illustrations. *Cal. Pre-U., 1961 ; '63*

9. Complete the following equations—

(*a*) $KOH+HNO_3=$

(*b*) $ZnSO_4+H_2S=$

(*c*) $CO_2+2Mg=2MgO+$

(*d*) $FeS+2HCl=$

(*e*) $Zn+H_2SO_4=$

(*f*) $CaCO_3=CaO+$

10. What is wrong with the following equations?

(i) $Mg+Cl=MgCl$

(ii) $CO_2+Ca(OH)_2=CaCO_2+2H_3O$

(iii) $KClO_3=KCl+O_2$

(iv) $Sn+Cl_2=SnCl_2$

(v) $2Fe+6HCl=3FeCl_3+3H_2$

11. Express the following statements by chemical equations :—

(i) Sulphur burns in oxygen giving sulphur dioxide.

(ii) Sodium decomposes water giving hydrogen and caustic soda.

(iii) Mercuric oxide on being strongly heated gives mercury and oxygen.

(iv) Nitrogen and hydrogen combine together to give ammonia.

CHAPTER VI

STRUCTURE OF AN ATOM AND ELECTRONIC THEORY OF VALENCY

The atom : Its Electronic Structure.—Recent experiments on Radio-activity, X-Ray spectrum, Positive rays, Disintegration of atoms etc., show that although the atom may still be regarded as *indivisible* so far as *chemical reaction is concerned*, strictly speaking, it is not so, and the atom is made up of *neutrons*, *protons*, *electrons and positrons*.

Electron.—The electron carries a unit negative charge of electricity and its mass is about 1 ÷ 1850th times that of the hydrogen atom. For practical purposes we can *neglect* the mass of an electron.

Proton.—The proton carries a unit positive charge of electricity and its mass is nearly equal to the mass of the hydrogen atom. The protons are much less mobile than the electrons. A proton is looked upon by modern scientists as 1 neutron *in close combination with 1 positron*.

Neutron.—It has a mass *nearly* that of a hydrogen atom (about 1·008) and it is electrically *neutral*. Its true nature has not been determined. It might be a very close union of 1 electron and 1 proton, or it might be 1 proton *minus* 1 positron.

Positron.—It is said to be the exact *counterpart* of the electron. Its mass is about 1 ÷ 1850th times that of the hydrogen atom but it carries unit *positive* charge of electricity.

Nuclear Structure of the Atom.—(1) The internal constitution of the atom resembles a *miniature Solar system* and consists of two parts, *a positively charged nucleus* (containing protons and neutrons) occupying a very small portion of the total volume of the atom resembling the sun, and a number of *extra-nuclear* electrons, resembling the planets revolving in orbits round the nucleus. These electrons are, therefore, called *planetary electrons* (also *called satellite electrons*). The greater part of the atom, however, is empty space.

(2) Since the mass of the electron is practically negligible, the whole mass of the atom must be concentrated in the nucleus, and it must be proportional to the number of neutrons and protons present in the nucleus.

(3) The simplest atom, *viz* the H-atom, contains only *one* proton in the nucleus.

(4) Since the atom is electrically neutral, it must contain as many protons as electrons; consequently, the net number of units of positive charges in the nucleus must be equal to the number of extranulear electrons. The number is called the atomic number.

(5) Since a proton or a neutron possesses a mass almost equal to that of the hydrogen atom, the atomic wt. of an element indicates the total mass of protons and neutrons present in the nucleus.

(6) The number of neutrons in the nucleus of an element is equal to its atomic weight *minus* its atomic number.

(7) Atoms of the same element, therefore, must contain the same number of net positive charges in the nucleus; while atoms of different elements contain different number of net positive charges in the nucleus.

(8) Though atoms of the same element must contain the same number of net positive charges in the nucleus, they *may* or *may not* contain the same number of neutrons.

Atomic Number.—The atomic number of an element is equal to the number of protons and hence also equal to the number of planetary electrons carried by an atom of that element.

Distribution of planetary electrons in different orbits.

The planetary electrons are distributed in different orbits around the nucleus.

There is a limit to the number of electrons which can be put in different orbits, the maximum number being given by the expression $2n^2$, where n is the number of the orbit starting from the nucleus.

Orbit number	Maximum electron capacity
1	$2\times1^2=2$
2	$2\times2^2=8$
3	$2\times3^2=18$
4	$2\times4^2=32$

There are two limitations to this rule :—

(1) The last orbit containing electrons can never hold more than 8 electrons whatever may be its number. Thus orbit number 3 can hold $2\times3^2=18$ electrons, only if there are electrons in orbit number 4. If it happens to be the outermost orbit to contain electrons, then it can hold upto the maximum limit of 8 electrons only.

(2) The last but one orbit containing electrons can hold not more than 18 electrons irrespective of its number. For example, orbit number 4 can hold upto $2\times4^2=32$ electrons, only if there are

example, all atoms having 17 protons are atoms of chlorine. It is now known that two atoms may have the same number of protons, but differ in the number of neutrons which they contain. These two atoms, therefore, represent two specimens of the same element having different atomic masses, as the mass of an atom is determined by the total number of protons and neutrons. They are said to be *isotopes*.

Isotopes.—*Two or more specimens of elements having the same At. number but different atomic masses, and occupying the same place in the periodic table, are called isotopes.*

Electronic theory of Valency.

What is the nature of the force which keeps the atoms bound together in a molecule ? Why should atoms of different elements possess different combining capacity or valency ? Nobody had any answer for questions like these, though it was vaguely suspected that the force of chemical affinity was electrical in nature. Now the electronic theory of valency based on atomic structure has been able to afford a very satisfactory explanation for all these facts. It is now definitely known that the valency of an element is exclusively an affair of its electrons and results from the tendency of its atoms to lose or gain electrons. Chemical union takes place by redistribution of electrons between participating atoms, the electrons in the outermost shell being mainly involved.

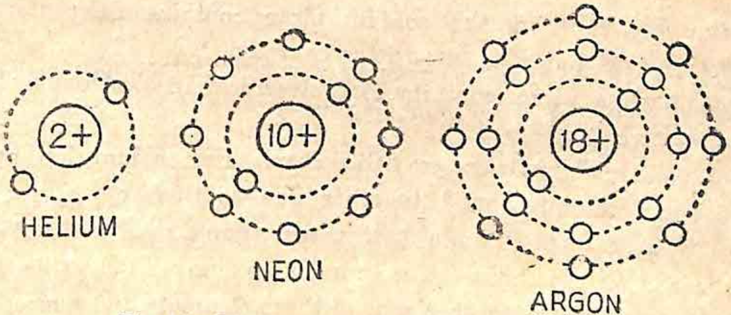


Fig. 21—Electronic structure of inert gases

The electronic structures of inert gas atoms are supposed to be the stablest. Having full quota of electrons in different shells, they have no tendency to gain or lose electrons which accounts for their chemical inactivity.

All the inert gases contain eight electrons (an octet) in their outermost shell except helium which has only two which is the maximum number its outermost shell can hold.

As all substances have a natural tendency to pass into stabler forms, the atoms of different elements tend to assume the stable electronic configurations of inert gases nearest to them in the periodic table. When chlorine and helium are mixed together, nothing happens because no transference of electrons can possibly take place between electrons in orbit 5 as well as in orbit 6. If there is no electron in orbit 6, the maximum number of electrons in orbit 4 is 18, provided there are electrons in orbit 5.

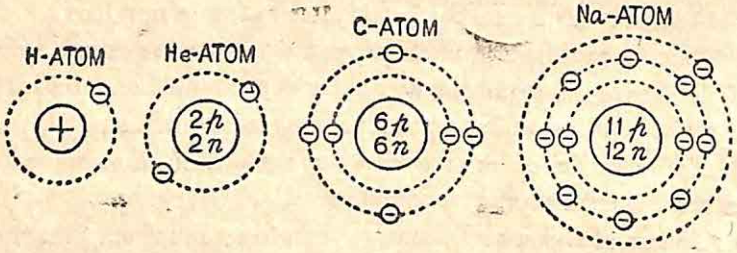


Fig. 20—Structure of some typical atoms.

Illustration—**Hydrogen Atom**—Since the mass of proton is *nearly* equal to that of the hydrogen atom, an atom of hydrogen cannot contain more than 1 proton. It contains 1 electron in orbit number 1. The At no. of hydrogen is 1.

Helium Atom.—At. wt. is 4, and the At. no. is 2. Therefore, we have 2 protons and 2 neutrons in the nucleus and 2 electrons both in orbit no. 1.

Carbon Atom—At. wt. is 12 and the At. no. is 6. There are 6 protons and 6 neutrons in the nucleus and 6 electrons in the outside orbits—2 in orbit no. 1 and 4 in orbit no. 2.

Sodium Atom—At wt. is 23. and the At. no. is 11. There are 11 protons and 12 neutrons in the nucleus and 11 electrons in the outside orbits—2 in orbit no. 1, 8 in orbit no. 2 and 1 in orbit no. 3.

Atomic Nuclei

Element	Carbon	Sodium	Chlorine	Calcium	Bromine	Lead
At. wt.	12	23	35	40	80	207
At. No.	6	11	17	20	35	82
Protons in the nucleus	6	11	17	20	35	82
Neutrons in the nucleus	6	12	18	20	45	125
Stucture of the nucleus	6*n* 6+	12*n* 11+	18*n* 17+	20*n* 10+	45*n* 35+	125*n* 82+

Isotope.—The chemical properties of an atom is exclusively determined by the number of protons in the nucleus, which is its atomic number. If the different atoms all carry the same number of protons, they are all atoms of the same element. For helium and any other atom. But when sodium and chlorine are brought together, they react to form sodium chloride. In this case one electron is transferred from the sodium atom to the chlorine atom. The sodium atom by losing an electron and the chlorine atom by gaining it assume the electronic pictures of the nearest inert gases, neon and argon respectively.

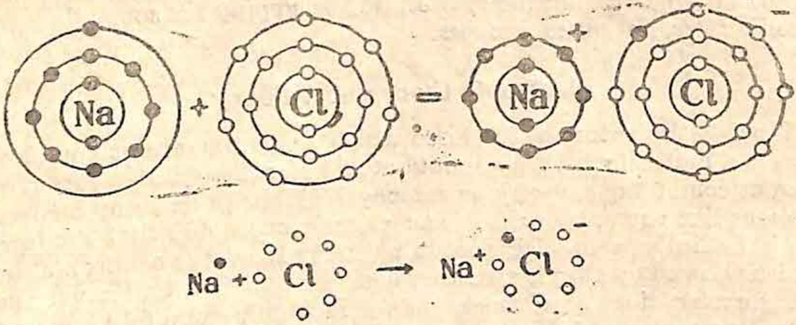


Fig. 22—Electronic Structure of Sodium Chloride molecule.

After the reaction, the sodium atom contains 11 protons and 10 electrons and hence a net positive charge of 1.

The chlorine atom contains 17 protons and 18 electrons and hence a net negative charge of 1.

These charged particles are called *ions*. The sodium ion and the chlorine ion remain bound together due to their opposite charges. They, however, form an ionic pair rather than a rigid molecule in the strict sense of the term. The ions of sodium and chlorine are very different from the neutral atoms of these elements and hence the resultant compound, sodium chloride has none of the properties of its constituent elements.

Consider also the formation of calcium sulphide. A calcium atom (2, 8, 8, 2) donates both the electrons in its outermost orbit to sulphur atom (2, 8, 6) whereby both the atoms possess the stable electronic structures characteristic of an argon atom (2, 8, 8).

This kind of valency which results from transfer of electrons between dissimilar atoms is known as Electrovalency.

Now this business of lending and borrowing of electrons cannot obviously take place between two similar atoms because the atoms being alike can either lend or borrow. They cannot possibly do both. Take the case of two chlorine atoms forming a molecule of chlorine. Both chlorine atoms want to borrow and not lend an electron. They have only 14 electrons between them in their last orbits. How can they complete their octets ? The chlorine atoms can meet their deficit of electrons by sharing of their electrons. Each chlorine atom allows one of its outermost electrons to be used by the other while retaining its share in it so that the pair of electrons becomes the joint property of both, the electrons counting towards the octet of each. Thus the two chlorine atoms are bound together by a pair of shared electrons to form a molecule of chlorine.

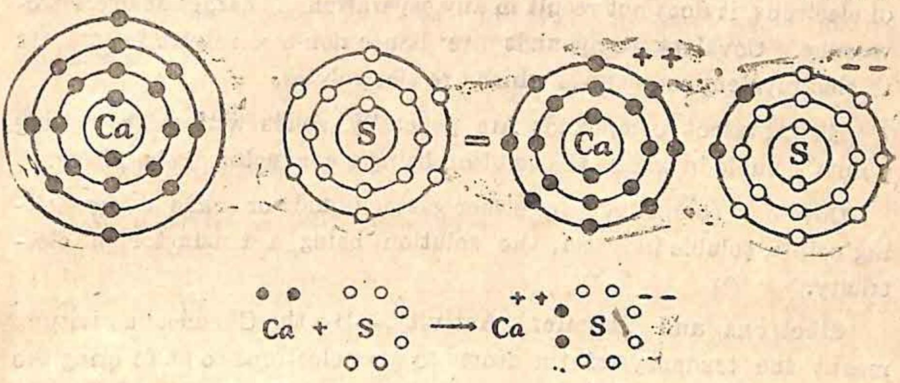


Fig. 23—Electronic Structure of Calcium Sulphide molecule.

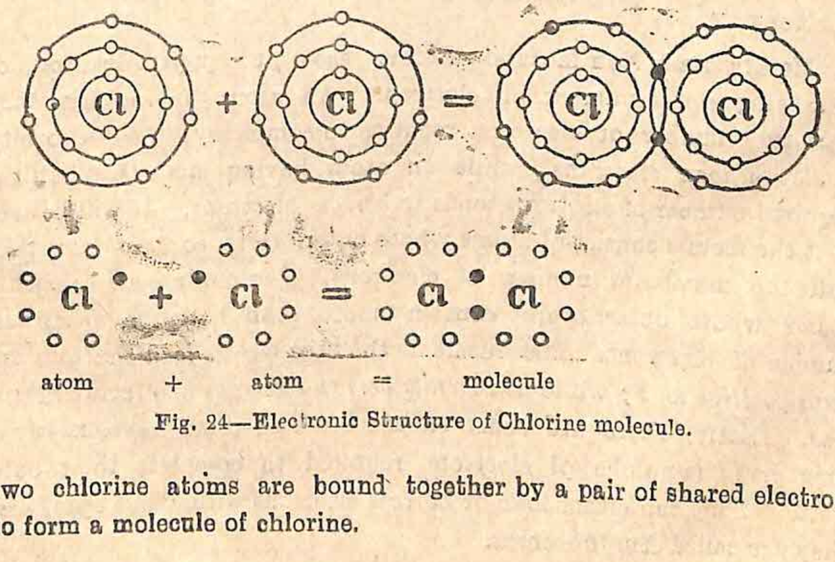


Fig. 24—Electronic Structure of Chlorine molecule.

The valency which results from sharing of electrons between similar atoms are known as Covalency.

Other examples of Covalency are found in water, hydrochloric acid and methane.

As the formation of a Covalency does not involve any gain or loss of electrons, it does not result in any separation of charges as in electrovalency. Covalent compounds are hence non-electrolytes in contrast to electrovalent compounds which are electrolytes.

Electrovalent compounds are generally solids with high melting points, soluble in water, the solution being a conductor of electricity.

Covalent compounds are either gases, liquids or solids of low melting points, soluble in water, the solution being a conductor of electricity.

Electrons and Chemical Activity.—By the Chemical activity is meant the tendency of the atoms to *gain* electrons so as to bring the number of electrons in the outermost shell up to 8, or to *lose* the few electrons residing on the outermost shell making the *next* complete inner shell to be the outermost shell. Now when an atom loses an electron, it becomes *positively* charged, while when it gains an electron, it becomes *negatively* charged.

Electro-positive character of an element is its *tendency* to lose electrons ; while **Electro-negative** character is its *tendency* to gain electrons.

Metals and Non-Metals.—Atoms seem to prefer loaning or borrowing small number of electrons. An atom having *less than* half the number of electrons required to complete its outer orbits, tends to *loan* electrons , while an atom having *more than* half the required number of electrons tends to *borrow* electrons. It will be seen that the metals consist of atoms whose outer orbits contain less than half the maximum number of electrons. The non-metals consist of atoms whose outer orbits contain more than half the maximum number of electrons. The result is that the *metals loan electrons* and form *positive ions ;* while *non-metals borrow electrons* and form *negative ions.* Lastly, there are some elements whose atoms have exactly or about half the number of electrons required to complete their outer orbits. They can either loan or borrow electrons with about *equal ease.* They are called **Amphoterics.**

Exercise.

1. How does the electronic theory account for covalencies and electrovalencies ?

2. Write electronic formulae for sodium chloride, methane, carbon dioxide and oxygen.

3. Give an account of the electronic theory of valency.
Delhi B.Sc., 1932, '41 ; Punjab, 1923, '41.

4. Explain and illustrate what you understand by electrovalency and covalency. Discuss the characteristic properties of electrovalent and covalent compounds.

5. What are your ideas regarding valency ? How can valency of an element be determined ? Clearly explain what you understand by covalency and electrovalency ?
C. U., 1947.

6. Explain the term "Atomic number" with illustrations.
Cas. Pre-U. 1961 ; '64.

7. Write short notes on the following :—
   (a) Atomic number
   (b) Protons and Electrons
Cal. Pre-U. 1966

CHAPTER VII

TERMINOLOGY AND CHEMICAL NOMENCLATURE : ACIDS, BASES AND SALTS.

Names of Elements : The names which have been given to the elements are not based on any particular scientific system. No hard-and-fast rule can, therefore, be laid down in this matter.

Many elements were given names signifying some of their properties etc. Thus, the name *chlorine* is derived from its *green* colour ; *bromine—bad smell* ; *barium*—from the *heaviness* of the mineral ; *argon*—from its *inertness* ; *strontium*—from a place in Scotland ; *uranium*—after the name of the planet Uranus ; *etc.*

It is customary to apply—

(1) names ending in **-um** to the metallic elements *e. g.*, **sodium**, **calcium**, **magnesium**, etc., and

(2) names ending in **-en**, **-ine**, **-on**, etc., to the non-metallic elements *e. g.*, **hydrogen**, **bromine**, **silicon**, **argon**, etc.

But this is not always the case. For example, the non-metals **selenium**, **tellurium** have names ending in **-um** while **sulphur**, **phosphorus**, etc., do not come under (2).

Names of Compounds.

Binary compounds.—They are compounds formed by the combination of two different elements.

They are the simplest of all compounds. The **names** of the binary compounds are made up of the names of the constituent elements and end in -'**ide**'. Thus—

CS_2	is	Carbon disulphide
CaO	is	Calcium oxide

When one of the elements is a **metal** or any other **electropositive** elements and the other a **non-metal,** the names of the **electro-positive** elements stand **first** and the termination '**-ide**' is added to the non-metal.

HCl	Hydrogen chloride
CaC_2	Calcium carbide
Na_2S	Sodium sulphide
Mg_3N_2	Magnesium nitride
ZnI_2	Zinc iodide

When the **same two** elements combine together to produce **more than one** compound, the compounds are distinguished from one another *either*—

(I) by employing a system of numerical prefixes **mono-**, **di- tri-**, **penta-**, etc. Thus we have

CO	Carbon **monoxide**
CO_2	Carbon **dioxide**
PCl_3	Phosphorus **trichloride**
PCl_5	Phosphorus **pentachloride**

or—(2) by using the suffixes **-ic** and **-ous**. That which contains a great portion of oxygen (or other non-metallic elements) is an **-ic** compound, while the suffix -'**ous**' is added to the compound containing less proportion of it. The prefix '**per-**' is sometimes added to indicate the presence of a higher proportion of the non-metallic element

N_2O	Nitrous oxide
NO	Nitric oxide
Na_2O_2	Sodium peroxide
$FeCl_2$	Ferrous chloride
$FeCl_3$	Ferric chloride
Hg_2O	Mercurous oxide
HgO	Mercuric oxide

The prefixes sub bin, proto, and sesqui have practically gone out of use. They are retained in medical books.

Different kinds of Binary Compounds

Oxide —It is a binary compound of any element and *Oxygen.*
Hydride —It is a binary compound of any element and *Hydrogen.*
Nitride —It is a binary compound of any element and *Nitrogen.*
Halide —It is a binary compound of any element and *Halogen.*
Carbide —It is a binary compound of any element and *Carbon.*
Sulphide —It is a binary compound of any element and *Sulphur.*
Phosphide—It is a binary compound of any element and *Phosphorus.*

and so on

Ternary Compounds—Compounds containing **three** different elements are called ternary compounds *e. g.*, Sulphuric acid, H_2SO_4.

Quaternary Compounds.—Compounds containing **four** different elements are called quaternary compounds *e g.*, Sodium hydrogen sulphate, $NaHSO_4$.

Acids, Bases and *Salts* are usually the most important examples of ternary and quaternary compounds. Halogen hydracids and metallic oxides are not **ternary** compounds. They are binary compounds. Before we take up the nomenclature of acids, bases and salts we must try to understand what they are.

Acids.

Def. of Acids.—An acid is a compound containing ***replaceable*** **Hydrogen, a part or whole of which may be replaced, directly or indirectly, by a metal or a group of elements acting like a metal, to produce a salt.**

An acid, if soluble in water, turns ***blue*** **litmus** ***red*** **; has, unless it be very weak, a sour taste ; gives Hydrogen-ions in aqueous solution ; and reacts vigorously with alkalis.**

Thus, Sulphuric acid is an Acid, for—

(1) it contains *two replaceable* Hydrogen atoms in the molecule ;

(2) these two atoms of Hydrogen may be replaced by a metal like Na, partially—giving $NaHSO_4$, or wholly—giving Na_2SO_4 ; or by a group of elements equivalent to a metal like (NH_4) also partially—giving $(NH_4)\,HSO_4$ or wholly—giving $(NH_4)_2\,SO_4$;

(3) it produces salts: the products $NaHSO_4$, Na_2SO_4, $(NH_4)\,HSO_4$, and $(NH_4)_2SO_4$ are *all salts* ;

(4) it is *soluble* in water, turns blue litmus red, has a sour taste, gives H-ions in aqueous solution, and reacts vigorously with alkalis.

Classification of Acids, Oxyacids, and Hydracids (1) Acids containing both Hydrogen and Oxygen are called **Oxyacides** such as Sulphuric Acid, H_2SO_4 : Phosphoric acid, H_3PO_4 ; Nitric acid, HNO_3, etc. (2) Acids containing Hydrogen and other non-metallic element or elements, but **not Oxygen**, are called **Hydracids.**

Hydrochloric acid, HCl ; Hydrocyanic acid, HCN ; Hydrosulphuric acid, H_2S, etc., are examples of Hydracids.

N. B.—Acids may also be classified *into* (A) *Organic acids* and *Inorganic* or *Mineral acids* ; (B) *Monobasic*, *Dibasic* and *Tribasic acids* : and (C) *Weak acids* and *Strong acids*.

Nomenclature of Acids.—(1) *Oxy-acids.*—For naming the Oxy-acids almost the same suffixes and prefixes are used as in the case of binary compounds. Thus the smaller proportion of Oxygen in the series of acids is distinguished by the termination **-ous** and larger proportion by **-ic**. When the series extends to several members, the prefix **hypo-** (means *below*) is added to the compound which contains the lowest proportion of Oxygen, and the prefix **per-** (means *above*) is added to that which contains the highest proportion of Oxygen. (2) *Hydracids*—The names of *hydracids* usually begin with the prefix **hydro-** and terminate in **-ic**. Thus we have—

(1) Chlorine Acids

Hydrochloric Acid	HCl	
Hypochlorous Acid	$HClO$	Oxy-acids of Chlorine
Chlorous Acid	$HClO_2$	
Chloric Acid	$HClO_3$	
Perchloric Acid	$HClO_4$	

(2) Bromine Acids

Hydrobromic Acid	HBr	
Hypobromous Acid	$HBrO$	Oxy-acids of Bromine
Bromous Acid	$HBrO_2$	
Bromic Acid	$HBrO_3$	
Perbromic Acid	$HBrO_4$	

(3) Iodine Acids.

Hydroiodic Acid	HI	
Hypoiodous Acid	HIO	Oxy-acids of Iodine
Iodous Acid	HIO_2	
Iodic Acid	HIO_3	
Periodic Acid	HIO_4	

(4) Nitrogen Acids.

Hyponitrous Acid	$H_2N_2O_2$
Nitrous Acid	HNO_2
Nitric Acid	HNO_3

(5) Sulphur Acids.

Hyposulphurous Acid	$H_2S_2O_4$
Sulphurous Acid	H_2SO_3
Thiosulphuric Acid	$H_2S_2O_3$
Sulphuric Acid	H_2SO_4
Persulphuric Acid	$H_2S_2O_3$

(6) Phosphorus Acids.

Hypophosphorous Acid	H_3PO_2
Phosphorous Acid	H_3PO_3
Phosphoric Acid	H_3PO_4
Metaphosphoric Acid	HPO_3
Pyrophosphoric Acid	$H_4P_2O_7$

(7) Important Acids of Boron.

Orthoboric Acid	H_3BO_3
Metaboric Acid	$H_2B_2O_4$
Pyroboric Acid	$H_2B_4O_7$

(8) Important Acids of Silicon.

Metasilicic Acid	H_2SiO_3
Orthosilicic Acid	H_4SiO_4

Base.—A base is a substance, usually the oxide or the hydroxide of a metal (or a group of elements equivalent to a metal), which can neutralize an acid to produce a salt and water only (—*Taylor*).

A base, when soluble in water, turns *red* litmus *blue*.

$$\underset{\text{base}}{CaO} + \underset{\text{acid}}{2HCl} = \underset{\text{salt}}{CaCl_2} + \underset{\text{water}}{H_2O}$$

$$\underset{\text{base}}{Zn(OH)_2} + \underset{\text{acid}}{H_2SO_4} = \underset{\text{salt}}{ZnSO_4} + \underset{\text{water}}{2H_2O}$$

$$\underset{\text{base}}{KOH} + \underset{\text{acid}}{HNO_3} = \underset{\text{salt}}{KNO_3} + \underset{\text{water}}{H_2O}$$

N. B.—It may be noted that certain substances are, for convenience, classified with the bases although they do not conform to the above definition. These are Ammonia, NH_3 and some of its organic derivatives. They form salts with the acids *without the formation of water*. *Strictly speaking*, NH_3 is *not* a base ; the true base is ammonium hydroxide, $NH_4(OH)$.

$NH_3 + HCl = NH_4Cl$ (*no water*) $\qquad \underset{\text{base}}{NH_4(OH)} + \underset{\text{acid}}{HCl} = \underset{\text{salt}}{NH_4Cl} + \underset{\text{'water'}}{H_2O}$

Hydroxides.—*Hydroxides* may be *looked upon* as chemical compounds of metallic oxides and water. They contain an atom of a metal or a radical united with one or more hydroxyl groups.

$$\underset{\text{Sodium oxide}}{Na_2O} + H_2O = \underset{\text{Sodium hydroxide}}{2NaOH}$$

Alkalis are soluble basic metallic hydroxides (—*Taylor*).

Characteristics of Alkalis.—(1) They are soluble in water and give (OH)-ions in aqueous solution ; (2) their aqueous solution—(*a*) conducts electricity, (*b*) possesses a soapy feeling and destroys organic matter, (*c*) turns *red* litmus *blue*, phenolphthalein *pink*, methyl orange, *yellow* ; (3) they react with acids giving salts and water only ;

and (4) they usually precipitate the hydroxides of metals when added to the solution of their salts.

N. B.—All alkalis are bases, but all bases are not alkalis. Caustic soda (NaOH), caustic potash (KOH), calcium hydroxide $Ca(OH)_2$, etc., are the most important alkalis known.

Salts.—A salt is a compound formed by the *partial* or *complete* replacement of the replaceable Hydrogen atom or atoms present in the **molecule** of an acid by a metal or a group of elements acting like a metal.

Acid	*H—partially replaced by a metal or a group*	*H—wholly replaced by a metal or a group*
HCl	×	NaCl
H_2SO_4	$KHSO_4$ or $NH_4H(SO_4)$	K_2SO_4 or $(NH_4)_2SO_4$

Nomenclature of Salts.—Salts are named after the names of acids from which they are formed. In the case of *oxy-acids*, if the name of the acid ends in *-ic*, the name of the salt will end in *-ate*; and if the name of the acid ends in *-ous*, the name of the salt ends in *-ite*. That is to say.

-**ic** acids give -**ate** salts;
-**ous** acids give -**ite** salts.

But in the case of *hydracids*, in naming the salts the prefix *hydro-* is dropped and the termination *-ic* is changed to *-ide*. Thus—

Oxy-acids	**Salts**
Sulphur*ic* Acid	Calcium sulph*ate*
Phosphor*ic* Acid	Sodium phosph*ate*
Nitr*ous* Acid	Ammon. nitr*ite*
Chlor*ous* Acid	Zinc chlor*ite*
Hydracids	**Salts**
*Hydro*fluoric Acid	Barium fluor*ide*
*Hydro*cyanic Acid	Lead cyan*ide*

Acid salts or Bi-salts.—When the Hydrogen atoms present in the molecule of an acid are only *partially* replaced by a metal, the resultant salt is called by the name of the metal and Hydrogen at the same time. It is also called an *acid salt* or a *bi-salt*. Thus—

Acid	Acid salt or bi-salt
Sulphuric acid→	Sodium **hydrogen** sulphate or **Acid** sodium sulphate or Sodium **bi**sulphate, $NaHSO_4$
Phosphoric Acid→	**Di**-sodium hydrogen phosphate, or **Acid** sodium phosphate, Na_2HPO_4.

Classification of salts.

Salts are of **three** kinds :—**Normal salts, Acid salts** and **Basic salts.**

Normal salt.—A salt produced by the displacement of all the replaceable Hydrogen atoms present in the molecule of the acid by a metal (or a group) is called a **normal salt** *e.g.*, KNO_3, Na_2SO_4, Na_3PO_4, etc.

Acid salt.—A salt produced by the displacement of a **portion** only of the replaceable Hydrogen atoms present in the molecule of an acid by a metal (or a group) is called an **acid salt.** Thus $NaHSO_4$, Na_2HPO_4 etc. are regarded as acid salts.

Basic salt.—A basic salt is produced by the reaction of an *acid* with a *higher proportion* of the base than is necessary for the formation of a normal salt. Thus—$CuCO_3, Cu(OH)_2$; $2PbCO_3, Pb(OH)_2$ (*White lead*) are examples of basic salts.

A basic salt may *also* be looked upon as formed by the partial replacement of the hydroxyl groups of a di-acid or a tri-acid base by an acid radical. Thus—

$$Pb(OH)_2 \ (\textit{Base}) \rightarrow Pb(OH)\ (NO_3)\ (\textit{Basic salt}).$$

Basicity of Acids.—The basicity of an acid is its power of *neutralizing* a base, and is *measured* by the number of replaceable hydrogen atom or atoms present in the molecule of the acid.

An acid which contains **one** atom of replaceable hydrogen in a molecule is called a **monobasic** *acid* e.g., HCl, HNO_3, $HCOOH$ (Formic acid), CH_3COOH (acetic acid), etc.

Acids containing **two** atoms of replaceable hydrogen in each molecule are called **dibasic** *acids* e.g., H_2SO_4, H_2CO_3 (carbonic acid), etc.

Those acids which contain **three** atoms of replaceable hydrogen in a molecule, are called **tribasic** *acids* e.g., H_3PO_4 (Phosphoric acid).

Monobasic acids like HCl, HNO_3, etc. form only **normal** salts and cannot form acid salts ; for they contain only one atom of replaceable hydrogen in a molecule in each case.

Acidity of Bases.—The acidity of a base is its power of *neutralizing* an acid, and is *measured* by the number of hydroxyl groups contained in a molecule of the base. Thus KOH, $NaOH$, etc. are *monoacidic bases* ; $Zn(OH)_2$, $Ca(OH)_2$, are *diacidic* bases, bismuth hydroxide, $Bi(OH)_3$, aluminium hydroxide, $Al(OH)_3$ are *triacidic bases.*

N. B.—When a base does not contain a (OH) group, then its acidity is measured by the number of molecules of a monobasic acid required to *just neutralise* one molecule of the base. Thus to determine the acidity of CaO, we allow it to neutralize by HCl. We find that 1 molecule of CaO requires for neutralization 2 molecules of HCl; and, as HCl is monobasic, the acidity of CaO must be two. Hence, CaO is diacidic.

Exercise.

1. Give the names of the substances corresponding to the following formulae; FeO, Na_2SO_4, KNO_3, NaOH, $NaHCO_3$, Cu_2O and KOH. Write down the formulae of ten compounds of Hydrogen with the non-metals (excluding Carbon).

2. Define 'salt'. How will you classify salts? Classify the following:—Sodium bi-carbonate, Copper chloride and Sodium nitrate. Has the reaction of a salt anything to do with the classification? *C. U. 1928, '34.*

3. What do you understand by the basicity of an acid? State the basicity of HNO_3 and H_2SO_4, giving reasons for your statement. *Pat., 1930.*

4. A metal *R* is divalent in its '*ous*' compounds and trivalent in its '*ic*' compounds. Give the names and formulae of its chlorides, nitrates, sulphates and carbonates.

5. What are Alkalis? What are their characteristics? Are all bases alkalis?

6. Point out five properties common to all acids. Under what condition can an acid be prepared by the action of another acid on its salts? Could you tell whether a solid is Na_2SO_4? How?

Explain—(*a*) acid. (*b*) base, (*c*) acid salt, (*d*) basic salt, *C. U. 1942.*

7. What are acids? State, with your reasons, which of the following substances you regard as an acid:—Ammonia, hydrogen chloride, carbon dioxide, hydrogen sulphate. How is an acid salt prepared? *C. Jun., 1924; C. U., 1924.*

8. Write short notes on acids, bases and salts. *Cal. Pre. U. 1961.*

9. What do the terms (*a*) acid, (*b*) base and (*c*) salt signify? Illustrate with examples. *Cal. Pre. U. 1964.*

10. What are normal salts and basic salts? Give two examples in each case. *Cal. Pre U. 1965.*

CHAPTER VIII

PHYSICAL PROPERTIES OF GASES AND VAPOURS

One important distinction between a gas on the one hand and a solid or a liquid on the other is that a gas alters *considerably* in volume for small changes of pressure and temperature. Hence, when we specify a quantity of a gas by volume, we always mention its temperature and pressure. Thus 10 c.c. of hydrogen means practically nothing if we forget to mention its temperature and pressure. For 10 c.c. of hydrogen at a particular temperature and pressure will not remain 10 c.c. but will occupy different volumes at *different* temperatures and under *different* pressures. Furthermore, the volume of a gas changes considerably for small changes of pressure, when the temperature remains constant; as also for small changes of temperature, when the pressure remains constant.

Relation between the pressure and volume of a given mass of a gas at constant temperature.

Boyle's Law.—It runs thus—*Temperature remaining constant, the volume of a given mass of any gas varies inversely as the pressure.*

That is to say, if the temperature be kept constant, the volume of a given mass of gas diminishes with the increase of pressure or increases with the diminution of pressure. When the pressure is *doubled*, the vol. of the gas is reduced to *one-half* ; pressure being reduced to *half*, the volume is increased to *double* the original volume.

Deduction of formula.—If P be the pressure and V be the volume of a given mass of a gas, then according to Boyle's law,

$$V \textit{ varies as } \frac{1}{P} \text{ (when the temp. is constant).}$$

$$\text{Or, } V = k \times \frac{1}{P} \text{ (where } k \text{ is a constant). Or } PV = k.$$

Let the pressure be changed to P_1 and the corresponding volume be V_1. Then $P_1V_1 = k$. But $PV = k$. $\therefore P_1V_1 = PV$.

Or, again, if a fixed quantity of a gas at constant temperature have volumes denoted by V_1, V_2, V_3, V_4 etc., under pressures denoted by P_1, P_2, P_3, P_4, etc., *respectively*, then, by Boyle's law,

$$P_1V_1 = P_2V_2 = P_3V_3 = P_4V_4 = \text{etc.}$$

Influence of Pressure on Density.

Boyle's law may also be stated in the terms of the *pressure* and *density* of the gas. Thus if a *given mass* of a *gas* has a volume V_1 and density D_1 under a pressure P_1 and a volume V_2 and density D_2 under a pressure P_2, then since the density of a gas varies *inversely* as its volume, we find

$$D_1 : D_2 = V_2 : V_1. \quad \text{But } P_1V_1 = P_2V_2. \quad \text{Or, } V_2 : V_1 = P_1 : P_2$$

$$\therefore \frac{D_1}{D_2} = \frac{P_1}{P_2}.$$

Or, the density of a gas at constant temperature is directly proportional to its pressure.

Problems

1. *The vol. of given mass of a gas is 10 litres measured at a pressure equal to that of a column of Mercury 73·8 cm. high. What will the volume become if the pressure changes to that of a column of Mercury 76 cm. high ?*

Let P_1, V_1 represent the initial pressure and volume, and P_2, V_2 the final pressure and volume. Then

$$73{\cdot}8 \times 10 = 76 \times V_2$$

$$\therefore V_2 = \frac{73{\cdot}8 \times 10}{76} = 9{\cdot}7 \text{ litres.}$$

2. *50 c.c. of air at Normal pressre is compressed to 38 c.c. Taking the temperature to remain constant, find the increase of pressure.*

Let P denote the *final* pressure. Then by Boyle's law, $P \times 38 = 760 \times 50$ (for *760 mm. is the Normal pressure*).

$$\text{Or, } P = 1000 \text{ mm.}$$

$\therefore$ the increase of pressure is $(1000 - 760) = 240$ mm.

3. *Half a litre of air under 360 mm. pressure is compressed to 200 c.c. Taking the temperature to remain constant, find the new pressure.*

Let the new pressure be P. Then,

$$P \times 200 = 500 \times 360. \quad \text{Or, } P = \frac{500 \times 360}{200} = 900 \text{ mm.}$$

4. *One litre of a gas is measured at 740 mm. What will the volume become at 760 mm. at constant temperature?*

Let V be the required volume. Then by Boyle's law,

$$1000 \times 740 = V \times 760. \quad \text{Or, } V = \frac{1000 \times 740}{760} = 973{\cdot}68 \text{ c.c.}$$

5. *The volume of a gas with some marble measures 100 c.c. at 760 mm. pressure. On raising the pressure to 1000 mm. the total volume becomes 80 c.c. What is the volume occupied by marble?*

Let V c.c. be the vol. occupied by marble alone. Then the vol. of the gas is $(100 - V)$ c.c. at 760 mm. and $(80 - V)$ c.c. at 1000 mm. There will be no change in the vol. of marble due to the increase of pressure, for it is a solid. Therefore by Boyle's law,

$$(100 - V) \times 760 = (80 - V) \times 1000$$

$$i.e.,\ 24V = 400. \quad \text{Or, } V = 16{\cdot}6 \text{ c.c.}$$

Relation between the Temperature and the Volume of a given mass of a gas at constant pressure.

Charles' law.—It runs thus :

Pressure remaining constant, the volume of a given mass of a gas increases or diminishes by 1/273*rd of its volume at 0°C for every increase or decrease in temperature of 1°C.* Therefore

1 vol. of a gas at 0°C will become $\left(1 + \frac{1}{273}\right)$ vols. at 1°C

... ... $\left(1 + \frac{2}{273}\right)$ vols. at 2°C

... ... $\left(1 + \frac{3}{273}\right)$ vols. at 3°C

... ... $\left(1 + \frac{t}{273}\right)$ vols. at t°C

In the same way, when the temperature is decreased.

1 vol. of a gas at 0°C will occupy $\left(1-\frac{1}{273}\right)$ vol. at -1°C

... ... $\left(1-\frac{2}{273}\right)$ vol. at -2°C

... ... $\left(1-\frac{3}{273}\right)$ vol. at -3°C

... ... $\left(1-\frac{273}{273}\right)$ vol. at -273°C

The Absolute Scale of Temperature : Absolute Zero.

Thus we see that at -273°C the gas occupies no volume. Of course no one has traced the rate of contraction of any gas to -273°C, and, in fact, all gases become liquid before they reach so low a temp. ; but since they behave, at the ordinary temperature, as if they would vanish, or, at least occupy insensible volume at -273°C, this temperature affords us a very convenient reference point in thermometry, and is known as the **Absolute Zero**.

Relation between the Absolute and the Centigrade Scales of Temperature.—Thus 0°C becomes 273° according to the Absolute scale, and 100°C becomes 373° Absolute. That is to say, any temperature on the Centigrade scale is converted into that on the Absolute scale by adding 273 to it. If T denotes a temperature on the Absolute scale and t on the Centigrade scale, then $T=t+273$.

Deduction of the Formula.—Let us suppose the vol. of a given mass of a gas to be V_0 c.c. at 0°C

V_1 c.c. at t_1°C

and V_2 c.c. at t_2°C

Then, according to Charles' law, the vol. V_0 c.c. at 0°C will become $V_0\left(1+\frac{t_1}{273}\right)$ c.c. at t_1°C and $V_0\left(1+\frac{t_2}{273}\right)$ c.c. at t_2°C.

But, by supposition, V_1 and V_2 are the volumes at t_1 and t_2 degrees respectively,

$$\therefore\ V_1=V_0\left(1+\frac{t_1}{273}\right)=V_0\left(\frac{273+t_1}{273}\right)=\frac{V_0T_1}{273}$$

$$\text{and } V_2=V_0\left(1+\frac{t_2}{273}\right)=V_0\left(\frac{273+t_2}{273}\right)=\frac{V_0T_2}{273}$$

where T_1 and T_2 are Absolute temps. Hence

$$\frac{V_1}{V_2}=\frac{T_1}{T_2}.$$

Charles' Law may, therefore, be stated thus :—*The volume of a given mass of a gas varies directly as its Absolute temperature, so long as the pressure remains constant.*

It may also be proved easily that pressure remaining constant, the *density* of a gas varies *inversely* as the *Absolute temperature.* Thus if D_1 and D_2 be the densities of a given mass of a gas at T_1 and T_2 degrees Absolute repectively, then, by Charles' Law.

$$\frac{D_1}{D_2}=\frac{T_2}{T_1}. \text{ Or, } D_1=D_2\times\frac{T_2}{T_1} \text{ (at const. pressure).}$$

Problems.

1. *Eight litres of a gas at 0°C are heated to 80°C. Find the volume taking the pressure to remain constant.*

Let V be the new vol. Then by Charles' law,

$$\frac{V}{8}=\frac{80+273}{0+273}. \text{ Or, } V=\frac{353\times 8}{273}=10\text{'}344 \text{ litres.}$$

2. *200 c.c. of Nitrogen at 27°C are cooled to—20°C. Find the new volume.*

Let V be the new vol. Then by Charles' law,

$$\frac{V}{200}=\frac{273-20}{273+27}. \text{ Or, } V=\frac{200\times 253}{300}=168\text{'}66 \text{ c.c.}$$

3. *Find the temperature at which 100 c.c. of air at 17°C will be double in its volume.*

Let $t°$ be the reqd. temp. Then by Charles' law,

$$\frac{100}{2\times 100}=\frac{273+17}{t+273}=\frac{290}{t+273}$$

$$\text{Or, } t+273=2\times 290. \text{ Or, } t=580-273=307°\text{C}$$

4. *The density of Nitrogen is 14 at 0°C. What is its density at −7°C ?*

Let D be the required density. Since the densities vary inversely as the Absolute temps. (—Charles' law).

$$\frac{D}{14}=\frac{273+0}{273-7}. \text{ Or, } D=\frac{273\times 14}{266}=14\text{'}36$$

Combined effect of Temperature and Pressure on the Volumes of Gases: General formula combining Boyle's and Charles' Laws.

Let V be the volume of a given mass of a gas at pressure P and at temperature T° *Absolute.* Let V_1 and P_1 be the volume and pressure of the *same* mass of gas at T_1° Absolute. Now

$$V\propto\frac{1}{P}, \text{ when T is constant (—Boyle's Law).}$$

$V \propto T$, when P is constant (—Charles' law).

$\therefore \quad V \propto \frac{T}{P}$, when both T and P vary.

Or, $V = \frac{T}{P} \times k$, where k is a constant. Or, $\frac{PV}{T} = \text{constant}$.

Similarly, $\frac{P_1V_1}{T_1} = \text{constant}$, and if P_2, V_2 ; P_3, V_3 ; P_4, V_4 ; P_n, V_n, etc. be the pressures and volumes of the same mass of gas at T_2, T_3, T_4, T_n, respectively,

$$\text{then, } \frac{PV}{T} = \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} = \frac{P_3V_3}{T_3} = \frac{P_4V_4}{T_4} = \text{etc.} = \frac{V_nP_n}{T_u}.$$

Standard Temp. and Pressure.—We have seen that the volume of a given mass of a gas varies according to the temp. and pressure to which it is subjected. Now the atmospheric temp. and pressure are constantly changing. In order, therefore, that the results of experiments involving volumes may be compared, it is necessary to reduce the volume to certain conditions of temp. and pressure. The standard values which have been agreed upon are 0°C and the pressure of the atmosphere equal to that of a column of Mercury 760 mm. high. These *standard conditions* are referred to as 'Standard Temp. and Pressure' (S. T. P.), or 'Normal Temp. and Pressure' (N. T. P.).

N. T. P.—It is the abbreviation for 'Normal Temp. and Pressure' and denotes 0°C and 760 mm. pressure.

Again, $\frac{PV}{T} = \text{constant} = R$ (*say*). This is known as the **'General Gas equation'**, and R is called the **'Gas Constant'**. When P=one atmosphere, V=gm. mol. vol. *i.e.*, 22·4 litres, and T=273, R=22·4÷273=·032 litre-atmosphere.

Combined effects of Temp. and Pressure on the Density of Gases.—

Let D be the density of a certain mass of a gas at temperature T° Absolute and at pressure P. Also let D_1 be the density of the *same* mass of the gas at temperature T_1° Absolute and P_1 pressure. Then,

$D \propto \frac{1}{T}$, when P is constant (—Charles' law)

and $D \propto P$, when T is constant (—Boyle's law)

$\therefore \quad D \propto \frac{P}{T}$, when both T and P vary

Or, $D = \frac{P}{T} \times k$, where k is a constant. Or, $\frac{DT}{P} = k$.

Similarly, $\frac{D_1T_1}{P_1} = k$. $\therefore \quad \frac{DT}{P} = \frac{D_1T_1}{P_1} = \frac{D_2T_2}{P_2} = \text{etc.}$

Relation between Temperature and Pressure.—We have seen that

for *all* gases $\frac{PV}{T} = \text{const.} = R$ (*say*). Or $P = \frac{RT}{V}$

Now, if the vol. be kept constant, then $\frac{R}{V}$ is constant $\therefore P \propto T$.

That is to say, *the volume of a certain mass of a gas being constant, its pressure varies directly as the absolute temp.*

$$\text{Hence, } \frac{P}{P_1}=\frac{T}{T_1}.$$

Problems.

1. *A gas occupies 100 c.c. at N.T.P. Find its volume at 27°C and 380 mm. pressure.*

Let V c.c. be the required volume. Then by the combination of Boyle's and Charles' laws, we find $\frac{PV}{T}=\frac{P_1V_1}{T_1}$,

Here $V=100$ c.c. V_1—to be determined.
$P=760$ mm. $P_1=380$ mm.
$T=(273+0)^\circ$ Abs. $T_1=(273+27)^\circ$ Abs.

$$\frac{100\times 760}{273}=\frac{V_1\times 380}{(27+273)} \quad \text{Or,} \quad V_1=\frac{100\times 760\times 300}{380\times 273}$$

$$=219{\cdot}78 \text{ c.c.}$$

2. *When the pressure is 760 mm. and the temperature 0°C, the volume of a gas is 910 c.c. What will be the volume at pressure 380 mm. and temperature 27°C ?*

Let V_1 c c be the required vol. Then, by the combination of Boyle's and Charles' laws, we have

$$\frac{PV}{T}=\frac{P_1V_1}{T_1}$$

Here $V=910$ c c. V_1—to be determined.
$P=760$ mm. $P_1=380$ mm.
$T=(273+0)^\circ$ Abs $T_1=(273+27)^\circ$ Abs

$$\therefore \quad \frac{910\times 760}{273}=\frac{V_1\times 380}{(273+27)} \quad \text{Or,} \quad V_1=\frac{910\times 760\times 300}{380\times 273}$$

$$=2000 \text{ c c.}$$

Dalton's Law of Partial Pressure.—*The pressure exerted by a mixture of gases and vapours (which do not react chemically with one another) occupying a certain volume at a given temp. is equal to the sum of the pressures which the constituents would exert if each had occupied separately the volume of the mixture at the temperature.*

The partial pressure of a gas or a vapour in a mixture, is the pressure which it would exert if it alone had filled the space in which the mixture is contained.

Mathematical Deduction.—Let a gas occupying the volume V_1 under pressure P_1 be mixed with another gas occupying the volume V_2 under pressure P_2. Therefore, the volume of the mixture becomes

(V_1+V_2). And let the pressure of the mixture be P, as also the *partial pressure* of the 1st *gas* f_1 and the *partial pressure* of the *2nd gas* f_2. As a result of mixing,

the vol. of *1st* gas becomes (V_1+V_2) under its partial pressure f_1,
the vol. of *2nd* gas becomes (V_1+V_2) under its partial pressure f_2,

$$\text{by Boyle's law, } f_1=\frac{P_1V_1}{V_1+V_2} \text{ and } f_2=\frac{P_2V_2}{V_1+V_2}.$$

But the *total* pressure (P) being equal to the sum of the partial pressures.

$$P=(f_1+f_2)=\frac{P_1V_1}{V_1+V_2}+\frac{P_2V_2}{V_1+V_2}$$

$$\text{Or, } P(V_1+V_2)=P_1V_1+P_2V_2.$$

Problem.

A vessel of capacity 400 c.c and filled with Chlorine under 80 cm. is connected by a narrow tube and a stop-cock with another vessel of capacity 250 c.c. filled with Nitrogen under 100 cm. What will be the pressure when the stop-cock is opened ?

Let P be the required pressure. After mixing, the volume of $Cl_2 = 400+250)$ c.c. Let P_1 be its partial pressure. Similarly, the vol. of $N_2=(400+250)$ c.c Let P_2 be its partial pressure.

$$\text{By Boyle's law, } P_1=\frac{80\times 400}{400+250}\text{cm. and } P_2=\frac{100\times 250}{400+250}\text{cm.}$$

$$\text{But } P=P_1+P_2=\frac{80\times 400}{650}+\frac{100\times 250}{650}=87{\cdot}69 \text{ cm.}$$

Moist Gases.—Gases are occasionally collected in the laboratory over water. They are, therefore, moist and are saturated with water-vapour. When the pressure of such a sample of gas is to be determined, we must make allowance for the pressure due to the saturated vapour. Suppose the Vol. of a gas, collected over water, to be V c. c. when the barometer reading is P and the temp. of the water is t°. Evidently, the atmospheric pressure (P) is *balanced* jointly by the pressure of the gas and that of aqueous vapour at t°. Taking the tension of aqueous vapour at t° to be f, we find—

P = pressure of the *moist* gas.
= pressure of the *dry* gas + tension of aqueous vapour at t°.
Or, pressure of the dry gas (i.e., its true pressure)
= pressure of the moist gas *minus* $f=(P-f)$.

N B.—The vol. of a given mass of a moist gas is greater than when it is dry.

Problem,

400 c.c. of Oxygen are collected over water at 17°C and 750 mm. pressure. What will be the volume of the dry gas under standard conditions? (Tension of aqueous vapour at 17°C is 14·4 mm.).

Pressure of Oxygen $=(750-14{\cdot}4)=735{\cdot}6$ mm.

Let V c.c. be the vol. of Oxygen at N.T.P. Then by Boyle's and Charles' laws combined, we find that

$$\frac{400\times(750-14{\cdot}4)}{273+17}=\frac{V\times760}{273}$$

$$\text{Or, } V=\frac{400\times735{\cdot}6\times273}{760\times290}=364{\cdot}46 \text{ c.c.}$$

Diffusion of Gases.—All gases tend to mix with one another. Thus, if in a large room a jar of Ammonia or Chlorine be opened, the presence of the gas may, owing to its powerful odour, be detected within a few seconds in every part of the room, notwithstanding the facts that the room is filled with air and Chlorine is much heavier than air. Similarly, if a jar of hydrogen is placed over a jar of oxygen, mouth to mouth, the two gases will be found to mix with each other after some time. Hydrogen, which is very light, partly descends into the lower jar and the heavier oxygen partly rises up into the upper jar. This intermingling goes on till a uniform mixture of hydrogen and oxygen is formed in both the jars—against the action of gravity.

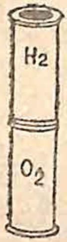


Fig. 25.—Diffusion

The natural process by which one gas is thus disseminated through another is called Gaseous Diffusion.

Graham's Law of Diffusion.—

The relative velocities of diffusion of gases (at constant temp. and pressure) are inversely proportional to the square root of their relative densities.

N. B.—By the velocity of diffusion of a gas, we mean the volume of the gas coming out per *unit* time.

If v vol. of a gas diffuses out in time t, then the velocity of diffusion of the gas $=\frac{v}{t}=\frac{\text{vol. coming out}}{\text{time}}$.

Let D_1 and D_2 represent the relative densities of two gases whose velocities of diffusion are V_1 and V_2 respectively, then by Graham's law,

$$V_1 \propto 1 \div \sqrt{D_1} \text{ and } V_2 \propto 1 \div \sqrt{D_2}$$

$$\text{Or, } V_1 = k/\sqrt{D_1} \text{ and } V_2 = k/\sqrt{D_2} \text{ where k is a constant}$$

$$\text{Or, } V_1\sqrt{D_1}=V_2\sqrt{D_2}.$$

The density of Hydrogen is unit and that of Oxygen is 16. If V_O and V_H be their velocities of diffusion respectively, then

$$V_O \times \sqrt{16}V = {}^{H} \times \sqrt{1}.$$

$$\text{Or, } \frac{V_O}{V_H}=\sqrt{\frac{1}{16}}=\frac{1}{4}.$$

$$\text{Or, } V_H=4\times V_O,$$

The velocity of diffusion of Hydrogen is four times the velocity of diffusion of Oxygen. In other words, Hydrogen diffuses *four* times as quickly as Oxygen does.

$$\text{Again, velocity of diffusion of } H_2=\frac{\text{vol. of } H_2 \text{ diffused}}{\text{time}}$$

$$\text{and, velocity of diffusion of } O_2=\frac{\text{vol. of } O_2 \text{ diffused}}{\text{time}}.$$

If v and v_1 be the respective vols. of H_2 and O_2 diffused and t and t_1 be the time required for diffusion, we have—

$$V_H=\frac{v}{t} \text{ and } V_O=\frac{v_1}{t_1}. \quad \text{But } V_H=4\times V_O \quad \therefore \quad \frac{v}{t}=4\times\frac{v_1}{t_1}.$$

Problems.

1. *The speeds of diffusion of Carbon dioxide and of Ozone were found by Soret to be as ·29 and ·271. The relative density of Carbon dioxide is 22 (when H=1). What is the relative density of Ozone?*

Bom., Punj. 1922; C. U., 1934.

Let Do be the relative density of Ozone. Then by the application of Graham's Law of Diffusion, we find—

$$V_{CO_2}\times\sqrt{D_{CO_2}}=V_O\times\sqrt{D_O}$$

$$\text{Or, } {\cdot}29\times\sqrt{22}={\cdot}271\times\sqrt{D_O}$$

$$\text{Or, } \sqrt{D_O}=\frac{{\cdot}29\times\sqrt{22}}{{\cdot}271}={\cdot}29\times4{\cdot}69\times3{\cdot}69$$

$$\text{Or, } D_O=(5{\cdot}02)^2=25 \text{ (approximately)}.$$

2. *100 c.c. of Hydrogen take 20 minutes to diffuse out of a vessel. How long will 40 c.c. of Oxygen take to diffuse under similar conditions?*

$$\frac{\text{Velocity of diffusion of } O_2}{\text{Velocity of diffusion of } H_2}=\sqrt{\frac{1}{16}}=\frac{1}{4}.$$

$$\text{But, velocity of diffusion of } O_2=\frac{\text{Vol. of } O_2 \text{ diffused}}{\text{time}}=\frac{v_1}{t_1}.$$

$$\text{And velocity of diffusion of } H_2=\frac{\text{Vol. of } H_2 \text{ diffused}}{\text{time}}=\frac{v}{t}$$

$$\therefore \frac{v}{t}=4\times\frac{v_1}{t_1}. \quad \text{Or, } t_1=4\times\frac{v_1}{v}\times t=\frac{4\times40\times20}{100}=32 \text{ minutes.}$$

3. In an expt. it was found that 500 c.c. of a gas A, diffused through a hole into a vacuum in the same time as 620 c.c. of air. Calculate the density of A relative to air.

By Graham's law,

$$\sqrt{\frac{\text{Density of A}}{\text{Density of air}}}=\frac{\text{Rate of diffusion of air}}{\text{Rate of diffusion of A}}$$

$$\therefore\ \frac{\text{Density of A}}{\text{Density of air}}=(620\div500)^2=1{\cdot}54.$$

Or, Density of A relative to air = 1·54.

Experiment to show that lighter gases diffuse more quickly than heavier gases.

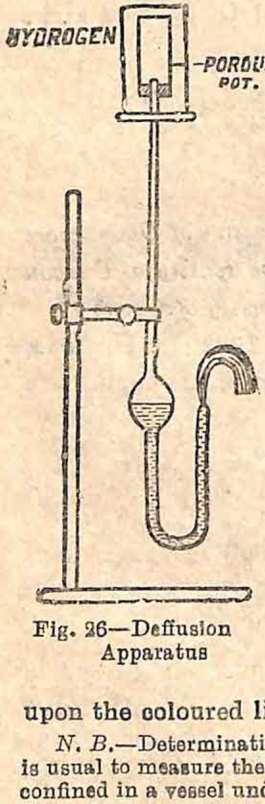


Fig. 26—Deffusion Apparatus

Take a porous cell (such as is used in voltaic batteries), fit it with an India-rubber stopper through which passes a long gas tube provided with a bulb and a fine jet at the outer end, and bent in the form of a U tube (fig. 26). Clamp the tube in a vertical position, detach the cell, and fill the lower part of the tube with coloured water. Replace the cell. The level of water is the same in both the limbs. Now invert a beaker filled with Hydrogen over the porous cell, when the coloured water rushes out of the fine jet in the form of a fountain. The reason is that hydrogen, being lighter than air, rushes in through the pores of the unglazed cell much more quickly than air can come out. Consequently, there is an increase in the number of gaseous molecules within the cell, with the result that greater pressure is exerted upon the coloured liquid which is forced out in the form of a fountain.

N. B.—Determination of the rate of diffusion of gases being *rather difficult*, it is usual to measure their rates of effusion. Effusion is the process of allowing gases confined in a vessel under pressure to escape through a small orifice (pin hole) or through some porous material such as a diaphragm of Plaster of Paris, unglazed porcelain (biscuit porcelain), or earthenware. Graham's Law holds good also in the case of *effusion*.

Exercise

1. Enunciate Boyle's Law. Describe an experiment which illustrates it. What do you understand by Absolute Zero and Absolute temperature?

A certain quantity of *dry* Hydrogen occupies 30 c.c. at 0°C and 720 mm. What will its volume become if the Hydrogen were saturated with moisture at 16°C, the atmospheric pressure being 759 mm.? **(Ans. = 29·95 c.c.)**

2. State Charles' Law. 60 cubic inches of Hydrogen originally measured at 20°C are cooled to -20°C. What will now be the volume of the gas?
All. 1904 [**Ans.** = 51·8 cubic inches]

3. Establish the relation between the temp., pressure and volume of a gas. How would you proceed practically to showt he effect of a change of temperature on the volume of a gas?
Punj., 1916 ; C. U., 1931, '34

4. What is the law of expansion of gases when they are heated at constant pressure? A flask can bear pressure up to 1·6 atmospheres. It is filled with Chlorine at 10°C and 764 mm. It is now heated till the flask explodes. At what temp. does the explosion take place?
[**Ans.** = 177·329°C]

5. A volume of Hydrogen measures 1 cubic decimetre at 20°C under a pressure of half-an-atmosphere. How many c.c. will it occupy at 10°C and 700 mm. pressure?
All., 1943. [**Ans.** = 524·329 c.c.]

6. When the pressure is 760 mm. and the temperature 0°C the volume of a gas is 910 c.c. What will be the volume of the gas when the pressure is 728 mm. and temp. is 27°C?
[**Ans.** = 1043·95 c.c.]

7. Calculate the temperature at which air possesses a density equal to that of Hydrogen at 0°C. (*Density of air* = *14·4*)
[**Ans.** = 3658·2°C]

8. The density of a gas is 14 at 27°C and 760 mm. What will its density be at 7°C and 740 mm.?
[**Ans.** = 14·61]

9. 0·5 gm. of Zinc dissolved in dilute H_2SO_4 gives 183 c.c. of Hydrogen at 9°C and 748 mm. What would the vol. be at N.T.P.?
[**Ans.** = 174·36 c.c.]

10. 10 c.c. of Hydrogen were measured at 20°C. What will the vols. be at 100°C, 180°C, and 200°C, the pressure being constant?
[**Ans.** = 12·78 c.c. ; 15·46 c.c. ; 16 14 c.c.]

11. What is Graham's Law of Diffusion?

Bom., 1925 ; Pat., 1928 ; All., 1913 ; Nag., 1933 ; C. U., 1932 ; Delhi, 1946.

The absolute density of Nitrogen is 1·25 gm./lit, and that of Hydrogen ·09 gm./lit. Calculate the volume of Nitrogen which would diffuse through a porous membrane of given area in the same time as 100 c.c. of Hydrogen.
[**Ans.** = 26·8 c.c.]

12. If 16 c.c. of Hydrogen diffuse in 100 seconds, what vol. of SO_2 will diffuse in the same time under similar conditions?
All., [**Ans** = 2·83 c.c.]

13. How many cubic centimetres of Hydrogen will pass through a porous plug in the same time as 1 c.c. of Air?
[**Ans.** = 379 c.c.]

14. Supposing that 374·2 c.c. of Hydrogen diffuse through a crack in 10 seconds, calculate how much Ethylene (C_2H_4) will diffuse in the same time.

[**Ans.** = 100 c.c.]

15. The relative rates of diffusion of HCl and C_2H_4 (Ethylene) are 167 and 191 respectively. Find the density of C_2H_4, given the density of HCl = 18·25.

[**Ans.** = 13·95]

16. Equal vols. of H_2 and CH_4 are placed in a porous vessel. H_2 diffuses from this at the rate of 1 litre per hour. What is the proportion of H_2 to CH_4 at the end of one hour?
All., 1919.

17. 6 c.c. of SO_2 diffused in 5·5 minutes while under the same conditions 68·8 c.c. of H_2S diffused in 4 minutes. What is the ratio of densities of those two gases?
[**Ans.** = 1·87 : 1]

18. The rates of diffusion of Ozone and Chlorine are as 6 : 5. Assuming the density of *Chlorine* as 36, find the Mol. formula of Ozone. (O=16, Cl=35·46)
Nag., 1931 [Ans. $=O_3$]

19. 180 c.c. of a Hydrocarbon diffuse in 15 minutes when 120 c.c. of sulphur dioxide (Mol wt. 64) diffuse in 20 minutes. What is the Mol. wt. of the Hydrocarbon ?
Nag., 1938. [Ans. = 16]

20. If 50 vols. of Hydrogen diffuse out of a vessel in 85 seconds, how long will 35 vols. of Nitrous oxide do so under the same conditions ? *All., 1936.*

CHAPTER IX

LAWS OF CHEMICAL COMBINATION OR STOICHEIOMETRY

Dalton's Atomic Theory and Avogadro's Hypothesis.

Laws of Chemical Combination or **Stoicheiometry are** altogether **five** in number. **Four** of them relate to combination of substances by **weight ;** and the **fifth,** to combination of gases **by volume :—**

1. *The Law of Conservation of Matter—(Lavoisier, 1789).*
2. *The Law of Constant Proportions—(Proust, 1799).*
3. *The Law of Multiple Proportions—(Dalton, 1803).*
4. *The Law of Reciprocal Proportions and the Law of Equivalent Proportions or the Law of Combining Weights—(Richter, 1792).*
5. *The Law of Gaseous Volumes—(Gay-Lussac, 1808).*

1. The Law of Conservation of Mass.—*When a chemical change occurs, the total mass of the reacting substances is equal to the total mass of the products.* (See indestructibility of matter, page 9).

For example, if masses m and n of substances A and B react to form masses x and y of substances C and D, then this law says that

$$m+n=x+y.$$

2. The Law of Definite or Constant Proportions.—*The same compound always contains the same elements combined together in the same proportions by weight.*

Thus, if the elements A and B combine together to form the compound AB, then in whatever manner AB is formed, it is composed of these two elements only. Also, if AB is formed in two different ways, and if in the first method a gm. of A unite with b gm. of B and in the second method x gm. of A unite with y gm. of B, then this law states that $a/b=x/y$.

Illustrations.—

(i) **Water** is a compound of **Hydrogen and Oxygen.** It can be obtained from various sources and can also be artificially prepared. Now the law of definite proportions says that from whatever sources we may get it, after proper purification, 9 parts by *weight* of water, on being analysed, will *always* be found to consist of 1 part by *weight* of Hydrogen and 8 parts by *weight* of Oxygen. And so long as the compound formed is water, this proportion by weight *shall* always remain *constant*.

(ii) Similarly, **Sodium chloride** can be prepared by *at least six different* methods. It can also be obtained from sea water and from dried-up lakes. Now when all the samples of NaCl after purification are analysed, it is found that in every case 35·46 parts by weight of Chlorine have combined with 23 parts by weight of Sodium to produce 58·46 parts by weight of Sodium chloride.

3. The Law of Multiple Proportions.—*When one element combines with a second element to form two or more different compounds, the weights of one of the elements which combine with a constant weight of the other, bear a simple ratio to one another.*

The meaning of Simple Ratio.—The expression *simple ratio* is used without any qualified terms to indicate the degree of simplicity. It is the ratio between *small whole numbers.*

Illustrations.—

(1) Hydrogen combines with Oxygen to form two different compounds, *viz* Water and Hydrogen peroxide. We see that

In water—

1 part by wt. of H has combined with 8 parts by wt. of O.

In hydrogen peroxide—

1 part by wt. of H has combined with 16 parts by wt. of O.

Thus, the weights of Oxygen (*viz* 8 and 16) which unite, in these cases, with the same weight of Hydrogen (*viz* 1) bear to each other the ratio 8 : 16 or 1 : 2.

(2) Similarly, Carbon and Oxygen combine together to give two oxides.

In Carbon monoxide—

1 part by wt. of Carbon combines with 1·33 parts by wt. of Oxygen.

In Carbon dioxide—

1 part by wt. of Carbon combines with 2·66 parts by wt. of Oxygen.

∴ the wts. of Oxygen *viz* 1·33 and 2·66 which combine with a constant wt. of Carbon (*viz* 1) are in the ratio of 1·33 : 2·66 *i.e*, as 1 : 2—which is a *simple ratio.*

4. The Law of Reciprocal Proportions.—*The weights of two or more different elements which separately combine with a definite weight of another element are either the same as, or are simple multiples of, the* *weights of these different elements when they combine amongst themselves.*

This Law is also known as the **Law of Equivalent Proportions.**

Illustrations.—

(i) Carbon and Oxygen combine with Hydrogen separately and also combine with each other. Let us take the compounds Methane (CH_4), Water (H_2O) and Carbon dioxide (CO_2) :

In CH_4, 12 gms. of Carbon unite with 4 gms. of Hydrogen.

In H_2O, 16 gms. of Oxygen unite with 2 gms. of Hydrogen.

or 32 gms. of Oxygen unite with 4 gms. of Hydrogen.

In CO_2, 12 gms. of Carbon unite with 32 gms. of Oxygen.

Thus, 12 gms. of Carbon combine with 4 gms. of Hydrogen to produce CH_4, and 32 gms. of Oxygen combine with 4 gms. of Hydrogen to form water. Therefore, if Carbon and Oxygen happen to combine together, they must do so either—(i) in the proportion of 12 : 32, or (ii) in its simple multiples. And in CO_2 we find that the two elements *do* combine in the proportion of 12 : 32.

(ii) In PCl_3, 31 parts by wt. of Phosphorus combine with
($3 \times 35{\cdot}46$) parts by wt. of Chlorine, and
In PH_3, 31 parts by wt. of Phosphorus combine with
3 parts by wt. of Hydrogen.

Therefore, if Hydrogen and Chlorine were to combine at all, they *would* do so in the proportion of $3 : 3 \times 35{\cdot}46$ or its simple multiples, and in HCl we find that they *do* combine in the proportion of $1 : 35{\cdot}46$.

5. **The Law of Gaseous Volumes** or **Gay-Lussac's Law**—*When gases combine together, they do so*—(i) *in simple ratios by volume ; and* (ii) *the volume of the product, if gaseous, also bears a simple relation to the volumes of the reacting gases, measured under the same conditions of temperature and pressure.*

Illustrations.—

1 vol. of Hydrogen and 1 vol. of Chlorine combine together to form 2 vols. of Hydrochloric acid gas.
(*ratio*—1 : 1 : 2)

2 vols. of Carbon monoxide and 1 vol. of Oxygen combine together to form 2 vols. of Carbon dioxide.
(*ratio*—2 : 1 : 2)

2 vols. of Hydrogen and 1 vol. of Oxygen combine together to produce 2 vols. of Steam.
(*ratio*—2 : 1 : 2)

1 vol. of Nitrogen and 3 vols. of Hydrogen combine together to form 2 vols. of Ammonia.
(*ratio*—1 : 3 : 2)

Thus, in every case, the volumes of the reacting gases bear a simple relation to one another and to the volume of the resulting product, which is also gaseous.

Dalton and Constitution of Matter.

John Dalton in 1808 adopted an ancient theory concerning the ultimate constitution of matter which had been expounded by the early Hindu and Greek Philosophers. They supposed that all substances where made of tiny particles too small to be visible and incapable of subdivision. Dalton developed it to the modern Atomic Theory to explain the Laws of Chemical Combination.

Dalton's Atomic Theory.—(1) Matter is discrete and is composed of minute particles called *atoms*, which do not undergo sub-division during chemical reactions and cannot be created or destroyed by any chemical process (—*Taylor*).

(2) Atoms of the *same* element are similar to one another in all respects and are equal in weight.

(3) Atoms of different elements have different weights and different properties.

N. B.—Thus all the atoms of Hydrogen are of equal weights and in other way alike and so are all the atoms of Oxygen : but an atom of Oxygen is sixteen times as heavy as an atom of Hydrogen and differs from it in all chemical and physical characters.

(4) Chemical combination between two or more elements takes place by the *union* or *juxtaposition* of the *atoms* of those elements in simple numerical proportions, *viz* 1 : 1 ; 1 : 2 ; 1 : 3 ; 2 : 3 ; etc.

Thus when two elements A and B combine together chemically, it is believed that one or more *atoms* of one element A become closely united with one or more *atoms* of the other element B. Hence, the smallest particle of water which can exist in the free state is believed to be made up of two atoms of Hydrogen united with one atom of Oxygen.

(5) The combining weights of the elements represent the combining weights of the atoms.

Dalton's Atomic Theory in the light of Modern Theory :

Modern views on atomic structure have greatly modified Dalton's theory. The important points where the modern theory differs from Dalton's theory are :—

(1) Atoms are no longer regarded as indivisible. It has been shown that they are composed of still smaller particles such as electrons, protons, neutrons etc. (see P. 42). Atoms of some elements break up spontaneously releasing some of these particles. Atoms of other elements can be smashed by special device. In ordinary chemical reactions, atoms, however, retain their individuality and do not break up.

(2) Atoms of the same element are not all alike. They may possess different mass, but they have the same atomic number and exactly the same chemical properties.

(3) Atoms of different elements may have the same mass, but they have different atomic number and differ in their chemical properties.

(4) The ratio in which atoms combine to form certain organic compounds cannot be regarded as simple. e.g. fat, $C_{57}H_{110}O_6$.

Dalton's Atomic Theory inspite of its defects, is still of value, as it can explain in a simple way the formation of compounds by the union of atoms of various elements and affords a simple explanation of the Laws of Chemical Combination.

Avogadro's Hypothesis.

What led to the adoption of Avogadro's Hypothesis.—Soon after Dalton had suggested the Atomic Theory, Gay-Lussac discovered, as a result of a large number of experiments, the Law of Gaseous Volumes. A few years before, the same chemist had discovered that all gases behave similarly with regard to changes of temp and pressure. It was at once seen that Dalton's Theory would provide a simple explanation of the facts discovered by Gay-Lussac ; and the *Theory* and *Law* could be harmonized. It was argued :—

(1) if elements in the gaseous state unite in simple proportions by volume (—*Gay-Lussac*) ; and

(2) if elements also unite in simple proportions by atoms (—*Dalton*), then

the number of atoms in equal volumes of the reacting gases must be simply related. And this relation was expressed by Berzelius thus—'*Equal volumes of different gases under corresponding condition of temperature and pressure contain the same number of atoms*'. (The word 'atom' was at that time used in the cases of both elements and compounds. Molecules had not yet been thought of). It was subsequently found that the Hypothesis was not tenable.

Why did the Hypothesis of Berzelius fail ?—The above hypothesis failed because it was based upon a *false reasoning*. Let us try to apply it to some specific cases.

Hydrochloric Acid Gas.

By actual experiment we find that—

1 vol. of Hydrogen combines with 1 vol. of Chlorine to give 2 volumes of Hydrochloric acid gas.

Let x be the number of *atoms* of Hydrochloric acid gas present in 2 volumes ; then by the hypothesis

1 vol. of Hydrogen will contain $\frac{x}{2}$ atoms of Hydrogen, and

1 vol. of Chlorine will contain $\frac{x}{2}$ atoms of Chlorine.

$\therefore$ $\frac{x}{2}$ atoms of Hydrogen combine with $\frac{x}{2}$ atoms of Chlorine to form also x atoms* of Hydrochloric acid gas.

---

*Dalton used the word 'matter' instead of 'element', and called the smallest particle of an element 'simple atom' and that of a compound 'compound atom'.

Or, ½ atom of hydrogen combines with ½ atom of Chlorine to form 1 atom of Hydrochloric acid gas.

But, according to Dalton, atoms cannot be divided.

Therefore, the hypothesis fails.

Avogadro pointed out that the difficulty could be got rid of by distinguishing between elementary atoms and the small particles of a gas. He recognisd two kinds of ultimate particles—

(i) The ultimate particles which can exist in the free state *e. g.* the smallest particles of gaseous Hydrochloric acid or Hydrogen. This is called **a Molecule.**

(ii) The ultimate particle that is capable of taking part in a chemical change or is capable of being transferred from one chemical compound to another *i. e.* the Hydrogen or Chlorine contained in a molecule of Hydrochloric acid gas. This is called an **atom.** Avogadro now corrected the above hypothesis thus :

Avogadro's Hypothesis—

Equal volumes of all gases (elementary and compound) under the same conditions of temperature and pressure contain the same number of molecules.

It means that when at a fixed temperature and pressure a vessel is successively filled with different gases, either elementary or compound, the vessel will contain *exactly* the *same* number of molecules in all cases.

The number of molecules in a *gram-molecule* of all gases is the same and is called *Avogadro's constant or Avogadro's Number.* It is $6{\cdot}06 \times 10^{23}$.

How Avogadro's Hypothesis helped in the development of the Atomic theory—Let us take up the case of **Hydrochloric acid gas** again and examine it *in the light of* **Avogadro's Hypothesis.** By actual experiment we find that—

1 volume of Hydrogen combines with 1 volume of Chlorine to form 2 volumes of HCl gas under same condition of temperature and pressure.

Let 'n' be the number of *molecules* present in 1 volume of H.

∴ 'n' molecules of Hydrogen combine with 'n' molecules of Chlorine to form '$2n$' molecules of HCl gas.

Or, 1 molecule of Hydrogen combines with 1 molecule of Chlorine to give 2 molecules of HCl gas.

For the present, we assume that a molecule of Hydrogen or a molecule of Chlorine is composed of two atoms.

∴ 2 atoms of Hydrogen combine with 2 atoms of Chlorine to give 2 molecules of HCl gas.

Or, 1 atom of Hydrogen combines with 1 atom of Chlorine to form 1 molecule of Hydrochloric acid gas.

This is not against the Atomic Theory, for though the atoms are indivisible, *the molecules can be divided.*

Dalton's Theory as modified by Avogadro's Hypothesis stands thus :

1. Substances (elements and compounds) consist of *molecules i.e.*, ultimate particles capable of separate existence ; and the molecules are composed of indivisible particles called *atoms*.

2. The molecules of a particular substance are similar to one another and possess the same properties and the same mass, but the molecules of one substance are altogether different from the molecules of another substance.

3. The molecules of an element consist of atoms which are all *alike*, while the molecules of a compound consist of atoms which are **not** all *alike*.

4. When chemical combination takes place between two or more substances, the molecules of each substance are first distintegrated into *atoms*, and then the atoms combine together in definite proportion to produce new molecules of the new substance or substances formed.

The merits, importance and usefulness of Avogadro's Hypothesis. How Avogadro's Hypothesis led to the development of Chemistry.—If the Atomic Theory is the splendid creation of a master mind, Avogadro's Hypothesis is none the less brilliant. It not only cleared up the difficulties which had puzzled Dalton, Berzelius and Gay-Lussac, and thus developed the Atomic Theory, but it gave a ready access to the determination of molecular weights. It cannot, of course, be verified by experiments, but consequences and conclusions, arising from it, have *always* been found to be true and in no case any result obtained from it has been found to be incorrect. In fact, Avogadro's hypothesis helped much towards the development of the Science of Chemistry. Thus—

(A) It for the first time used the word 'molecule' and made the **distinction** between **atoms** and **molecules.**

(B) **It explained** clearly Gay-Lussac's **Law of Gaseous Volumes** and led to the following important deductions.

Deductions from Avogadro's Hypothesis

(1) A molecule of Hydrogen or a molecule of Chlorine consists of two atoms (*—The formula of Hydrogen and Chlorine*).

By actual experiment we find that—

1 vol. of H combines with 1 vol. of Cl to give 2 vols. of Hydrochloric acid gas.

Let 'n' be the number of molecules present in 1 vol. of H or Cl.

∴ 'n' molecules of Hydrogen combine with 'n' molecules of Chlorine to give '$2n$' molecules of Hydrochloric acid gas.

Or, 1 molecule of Hydrogen combines with 1 molecule of Chlorine to give 2 molecules of Hydrochloric acid gas.

Now, since Hydrochloric acid gas is a compound of Hydrogen and Chlorine only, each molecule of Hydrochloric acid gas must contain *at least* 1 atom of Hydrogen and 1 atom of Chlorine. Therefore, in 2 molecules of Hydrochloric acid gas there must be present *at least* 2 atoms of Hydrogen and 2 atoms of Chlorine ; and these 2 atoms of Hydrogen must have come from 1 molecule of Hydrogen and 2 atoms of Chlorine must have come from 1 molecule of Chlorine. Hence, a molecule of Hydrogen or a molecule of Chlorine consists of *at least two* atoms.

Again, since Hydrogen present in the molecule of Hydrochloric acid gas can be replaced by a metal like Sodium in *one instalment* only, giving a normal salt ; and in no case, in *more than one* instalment (unlike H_2SO_4, H_2CO_3 and H_3PO_4 which give acid salts also) we are forced to believe that 1 molecule of HCl contains 1 atom of Hydrogen. Similar is the case with Chlorine. Hence, it follows from the above reasonings that 1 molecule of Hydrogen or 1 molecule of Chlorine consists of 2 atoms. Therefore, the formulas of Hydrogen and Chlorine are H_2 and Cl_2 respectively.

A Molecule of Oxygen is diatomic (*The Formula of Oxygen*).—We know that 2 vols. of Hydrogen combine with 1 vol. of Oxygen to give 2 vols. of steam. Applying Avogadro's Hypothesis we can show, in the above manner, that a molecule of Oxygen consists of *at least* two atoms of Oxygen. Now, the Oxygen present in a molecule of steam can be replaced by Chlorine in *one instalment only*, and in no case, in more than one instalement. Hence, we are led to believe that a molecule of steam contains 1 atom of Oxygen. Therefore, 1 molecule of Oxygen is made up of 2 atoms of Oxygen, and its *formula is* O_2.

In like manner, it may be proved that a molecule of any one of the **elementary gases** like Nitrogen, Fluorine, etc., (*except Ozone and the inert gases*) is *also* diatomic.

(2) **Mol. wt. of any gas is twice its Density (relative to Hydrogen).**—The density of a gas is the ratio of the weight of a certain volume of that gas to the weight of the *same* volume of Hydrogen, both measured under like conditions of temperature and pressure. Taking D as the density of a gas, we find—

$$D = \frac{\text{Wt. of } x \text{ volume of the gas}}{\text{Wt. of } x \text{ volume of Hydrogen}} \quad \text{(under the same temp. and pressure).}$$

Let 'n' be the number of molecules present in x vol. of the gas. Therefore, by Avogadro's hypothesis,

$$D=\frac{\text{Wt. of '}n\text{' molecules of the gas}}{\text{Wt. of '}n\text{' molecules of Hydrogen}}$$

$$=\frac{n\times\text{wt. of 1 molecule of the gas}}{n\times\text{wt. of 1 molecule of Hydrogen}}$$

$$=\frac{\text{Wt. of 1 molecule of the gas}}{\text{Wt. of 1 molecule of Hydrogen}}$$

$$=\frac{\text{Wt. of 1 molecule of the gas}}{\text{Wt. of 2 atoms of Hydrogen}}$$

(∵ Hydrogen mol. is *diatomic*)

$$=\frac{\text{Wt. of 1 molecule of the gas}}{2\times\text{wt. of 1 atom of Hydrogen}}$$

$$\text{Or,}\quad 2\times D=\frac{\text{Wt. of 1 molecule of the gas}}{\text{Wt. of 1 atom of Hydrogen}}$$

$=$Mol. wt. of the gas (—*by definition*).

N. B.—To find out the Mol. wt. of *any* gas, determine its density $(H=1)$ by actual experiment and multiply the density by 2.

(3) The Gm-molecular volume of all gases is the same under like conditions of temp. and pressure and is 22·4 litres at N. T. P.

(4) Determination of the Molecular Formula of a gas from its Volumetric Composition.—With the help of Avogadro's hypothesis we can fix the Moleculer Formula of a gaseous compound from its volumetric composition and density. Let us take the case of **Hydrogen Chloride.**

By actual experiment we find that 1 vol. of Hydrogen combines with 1 vol. of Chlorine to give 2 vols. of Hydrochloric acid gas.

Let n be the number of molecules present in one vol. of H.

∴ n molecules of Hydrogen combines with n molecules of Chlorine to give $2n$ molecules of Hydrogen chloride—(*Avogadro*).

Or, 1 molecule of Hydrogen combines with 1 molecule of Chlorine to give 2 molecules of Hydrochloric acid gas.

Or, 2 atoms of hydrogen combine with 2 atoms of Chlorine to give 2 molecules of Hydrochloric acid gas (—for H and Cl molecules are *diatomic*).

Or, 1 atom of Hydrogen combines with 1 atom of Chlorine to give 1 molecule of Hydrochloric acid gas.

Hence, the formula of Hydrochloric acid gas is HCl.

Confirmation of the formula HCl.—The density of Hydrogen chloride is 18·23.

∴ its Mol. wt. is $2\times 18{\cdot}23=36{\cdot}46$, which agrees with the formula HCl.

In a similar way, the Molecular formula of steam or water (H_2O), Carbon dioxide (CO_2) and of other gases can be determined from their volumetric compositions with the help of Avogadro's hypothesis (See Volumetric compositions of steam and Carbon dioxide, Chapters XV and XX).

(5) **Determination of At. Wts. of elements**—see Chapter X.

Exercise.

1. Explain fully the laws of Chemical combination giving one example in each case. What relation do they bear to the Atomic Theory?
Bom., 1919, '31; Punj., 1939; Mad., 1939. C. U., 1909, '11, '31, '33, '44

2. Enunciate Avogadro's law and explain its importance in determining the atomic weights of elements, illustrating your answer by examples.
Pat., 1928, '29; Mad., 1931, '37; C. U., 1915, '19, '32, '43, '45.

3. Define the law of Gaseous Volumes and illustrate it. What hypothesis was propounded to account for the facts underlying the law?
All., 1937; Mad., 1931; Punj., 1918, '35: C. U., 1915, '33, '44, '47, '49.

4. What is Avogadro's Hypothesis? Discuss the evidence on which it is based. What are the important deductions that can be made from it?
Bom., 1926; All., 1927; Pat., 1924; Punj., 1938; Nag., 1922; C. U. 1930, '37, '47, '49; Mad, 1931.

5. A molecule of Hydrogen, Nitrogen or Oxygen is said to consist of two atoms. Give reasons for the truth or otherwise of the statement.
C. U., 1943, '47; Pat., 1907; All., 1902. B. C. S. 1937.

6. Define the law of Multiple Proportions. Give at least two examples by which you can establish its truth. *Mad., 1931; C. U., 1938, '40, '49*

7. State the laws of Multiple and Reciprocal Proportions. PH_3 contains 91·1% of P and 89% of H; water contains 88·8% of O and 11·2% of H; and P_2O_3 contains 56·4% of P and 43·6% of O. Show, without using at. wts., that this data illustrate the law of Reciprocal Proportions. *Bom., 1934*

8. Write short notes on Dalton's Atomic Theory.
Punj.. 1932; C. U., 1917, '29, '42. Cal. Pre-U. 1961.

9. State and explain Avogadro's hypothesis. Deduce from it the relation between the molecular weight of a gas and its relative density with respect to hydrogen taken as unit. *Cal. Pre-U. 1961, '66*

10. State the law of Equivalent Proportions. *C. U., 1941*

11. State the law of Constant Composition. *Banaras., 1937: C. U., 1940*

12. 0·46 gm. of Mg gives 0·77 gm. of MgO; 0·82 gm. of Mg liberates 760 c.c. of H_2 at N.T.P. from acids. Show that the results illustrate a law of chemical action.
All., 1932.

13. State and explain the Law of Multiple Proportions.

Two oxides of an element are found to contain 36·84 and 46·67 per cent of the element respectively. Show that these figures are in accordance with the above law.
Cal. Pre-U. 1962; '67

14. State Avogadro's hypothesis. How would you determine the atomic weight of an element by the application of this hypothesis? *Cal. Pre-U. 1963.*

15. State and ecplain the Law of Conservation of Mass.

A piece of charcoal when burnt in air, loses in weight but a piece of magnesium gains in weight on burning in air. How would you reconcile the above facts with the Law of Conservation of Mass? *Cal. Pre-U. 1963.*

16. Explain with illustration—"Gay Lussac's Law of Gaseous volumes."
Cal. Pre-U. 1964.

17. State and explain fully the Laws of Chemical Combination (by weight) giving one example in each case. *Cal. Pre-U. 1965.*

CHAPTER X

CHEMICAL EQUIVALENTS, ATOMIC WEIGHTS AND MOLECULAR WEIGHTS

The idea of each element having a combining or equivalent weight follows directly as a corrolary of the Law of Reciprocal proportions.

Let the fixed weight referred to in the Law be 8 gms. of Oxygen.

Let the weights of different elements which separately combine with this weight of Oxygen be accurately determined and set down as follows.

8 gms. of Oxygen combine with
- 1·008 gms of Hydrogen
- 3 gms. of Carbon
- 12·16 gms. of Magnesium
- 20 gms. of Calcium
- 100·30 gms. of Mercury
- 35·46 gms. of Chlorine
- 80 gms. of Bromine
- 107·88 gms. of Silver
- 127 gms. of Iodine
- and so on.

According to the Law of Reciprocal Proportions, the numbers in the right hand column give the proportions in which the elements combine amongst themselves. These numbers which are called the **equivalent weights** of elements are useful for the day to day work of a chemist, for he can find by referring to this table in what proportions by weight he is to make certain elements combine to produce a particular compound.

For example, to prepare a compound of Mercury and Iodine (Mercuric iodide), he finds that he is to take for every 100·30 parts of Mercury, 127 parts of Iodine. Again, to prepare a compound of Silver and Chlorine (Silver Chloride), he is to take the weights of Silver and Chlorine in the ratios of 107·88 : 35·46 or simple multiples thereof.

Definition—The equivalent weight of an element is a number which shows how many parts by weight of the element combine with or displace from a compound 8 parts by weight of Oxygen or its equivalents, namely 1·008 parts by weight of Hydrogen or 35·46 parts by weight of Chlorine.

Illustrations. (1) 1·008 parts by weight of Hydrogen combine with 35·46 parts by weight of Chlorine to form Hydrochloric acid. Hence, the equivalent weight of Chlorine is 35·46.

(2) 12·16 parts by weight of Magnesium displace 1·008 parts by weight of Hydrogen from dilute sulphuric or hydrochloric acid. Hence, the equivalent weight of Magnesium is 12·16.

Hydrogen Versus Oxygen Standard of Equivalents.—The unit mass of Hydrogen was once taken as the standard for fixing the equivalent weights of other elements, for Hydrogen combines in smaller proportion by weight than any other element. In fact, Hydrogen has the smallest equivalent weight.

Now, however, comparison is made not with Hydrogen but with Oxygen, for many elements do not combine directly with Hydrogen nor displace it from a compound ; but most elements do so with Oxygen. Hence, the Eq. wts. of other elements are now expressed in terms of the Eq. wt. of Oxygen=8.

On this scale, the Eq. wt. of Hydrogen is not 1 but **1·008**.

Equivalent Wt. of an Element may vary.—When an element combines with Hydrogen, Oxygen, Chlorine. etc. giving, in each case, only *one compound*, its Eq. wt. is *constant*. But when an element combines with Hydrogen, Oxygen Chlorine, etc giving, in each case, more than one compound, its Eq. wt. will not then be constant. It will vary. Thus, Copper combines with Oxygen to give two compounds, viz. *red oxide of Copper*, Cu_2O and *black oxide of Copper*, CuO. Now, in the *first* compound 63·5 parts by wt. of Copper combine with 8 parts by wt. of Oxygen ; and in the *second* compound 31·75 parts by wt. of Copper combine with 8 parts by wt. of Oxygen. Therefore, Copper has two equivalents, 63·5 and 31·75.

Determination of Eq. Wts. of Metals.

1. Replacement of Hydrogen from Acids by Metals :

To Find the Equivalent Wt. of Magnesium—Accurately weigh out a piece of chemically pure Magnesium (about 0·2 gm.) in a watch glass and place it in a beaker of water. Cover the metal with a small funnel, taking care to see that the stem of the funnel remains completely immersed under water. Fill a graduated tube, closed at one end, with water and invert it over the funnel so that the stem of the funnel remains inside the tube. Add moderately *conc.* sulphuric acid to the water in the beaker. This acid slowly enters inside the funnel and when it comes in contact with Magnesium, Hydrogen gas is set free and collects inside the graduated tube in the form of bubbles (Fig. 27).

$$Mg + H_2SO_4 = MgSO_4 + H_2.$$

When the piece of Magnesium has completely dissolved in the acid, remove the tube by carefully closing the open end with the thumb, and plunge in into a tall jar of water. Bring the surface of water inside and outside the tube to the same level by holding the tube with a clamp or a piece of paper and not with the fingers (*for the warmth of the hand will expand the gas*) (Fig. 28), and carefully read out the vol. of Hydrogen. Note down the temp. of the room and the atmospheric pressure.

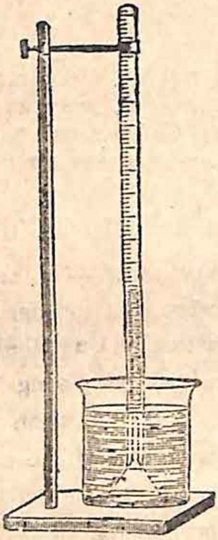


Fig. 27—Eq. Wt. Experiment

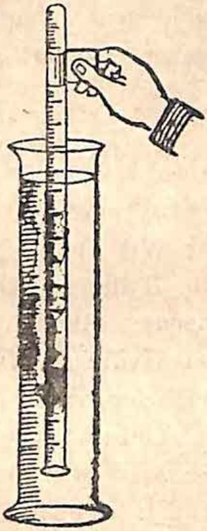


Fig. 28—Eq. wt. Experimant

Let the wt. of Magnesium taken be w gms., the vol. of Hydrogen V c c., the temp. of the room $t^\circ C$, and the atmospheric pressure P. Let the tension of aqueous vapour at $t^\circ C$ be f.

Calculation.—Since Hydrogen is collected over water, it is *moist*. Therefore, the atmospheric pressure (P) is *balanced* by the pressure of Hydrogen + tension of water-vapour (f) at $t^\circ C$. Or, P=Pressure due to dry Hydrogen + f Or, *Pressure of dry Hydrogen* $= (P - f)$.

Hence, by dissolving w gms. of Magnesium in *dil.* H_2SO_4 we have obtained V c.c. of Hydrogen at $t^\circ C$ and $(P - f)$ pressure. We must find the *weight* of this vol. (*viz* V c.c.) of Hydrogen.

Let V c.c. of Hydrogen at t°C and $(P-f)$ pressure occupy V_1 c.c. at N. T. P. Then, by the combination of Boyle's and Charles' Laws, we find

$$\frac{V(P-f)}{t+273}=\frac{V_1 \times 760}{273}$$

$$\text{Or,} \qquad V_1=\frac{V(P-f)\times 273}{760(t+273)} \text{ c. c.}$$

And its weight $=\frac{V(P-f)\times 273}{760(t+273)}\times {}^{\cdot}00009$ gms. (for 1. c.c. of Hydrogen at N. T. P. weighs ·00009 gm.). Hence,

$$\text{Equivalent Wt. of Mg}=\frac{\text{Wt. of Magnesium}}{\text{Wt. of Hydrogen liberated}}\times 1{\cdot}008$$

$$=\frac{w\times 760(t+273)}{V(P-f)\times 273\times {}^{\cdot}00009}\times 1{\cdot}008$$

The equivalent weights of **zinc, iron, aluminium** and **tin** may be determined by the above method.

N. B. Since pure zinc does not react with acids, a few drops of copper sulphate solution must be added to the dilute acid in the beaker to start the reaction.

2. Conversion of the metal into its oxide.—The method consists in converting a known weight of the metal into its oxide.

The conversion of the metal into its oxide may be done *directly* by burning completely a weighed quantity of the metal in oxygen or if that is not practicable, *indirectly* by dissolving the same in nitric acid and then heating the nitrate of the metal formed till it is completely decomposed into its oxide.

Direct. : Metal + Oxygen = Oxide of the metal

$$\text{Indirect. : Metal} \xrightarrow{HNO_3} \text{Nitrate of the metal} \xrightarrow{\text{heated}} \text{Oxide of the metal}$$

Calculation.—Let

wt. of the metal taken $= w$ gms.

wt. of the oxide formed $= w_1$,,

Hence the weight of the Oxygen which has combined with the metal $=(w_1-w)$ gms.

Hence, Eq. wt. of the metal

$$=\frac{w}{w_1-w}\times 8.$$

The direct formation of oxide method is possible with metals like **magnesium,** which are easily combustible. The indirect method is used in finding the Eq. Wt. of **copper, tin, zinc** and **iron.**

Eq. Wt. of Copper.—Determine the *constant wt.* of a porcelain crucible with its lid in a balance. Place a piece of *pure* Copper wire in the crucible and weigh it. Now add *conc.* Nitric acid to Copper drop by drop till the metal is completely dissolved. Keep the crucible nearly covered during the reaction. Evaporate the solution on a water-bath, taking care to see that there is no loss by spirting. The green residue left is Copper nitrate. Now, strongly heat it over a Bunsen flame till Copper nitrate is completely converted into black Copper oxide. Cool the crucible in a desiccator and weigh again. Repeat the processes of heating, cooling in a desiccator, and weighing, till the final weight is constant.

Calculation—Let

wt. of the crucible + lid $= w$ gms.

wt. of the crucible + lid + Copper $= w_1$ gms.

$\therefore$ wt. of Copper taken $= (w_1 - w)$ gms.

Final wt. of the crucible + lid + Copper oxide $= w_2$ gms.

$\therefore$ wt. of Oxygen combined with $= (w_2 - w_1)$ gms.

Hence, $(w_2 - w_1)$ gms. of Oxygen combine with $(w_1 - w)$ gms. of Copper to form Copper oxide. Therefore, 8 gms. of Oxygen will combine with

$$\frac{8(w_1 - w)}{(w_2 - w_1)} = \text{Equivalent wt. of Copper.}$$

3. Reduction of the oxide of the metal to the metal.—In this method, a known weight of a pure sample of the oxide of the metal is reduced completely by a suitable method such as heating in hydrogen or coal gas and the amount of metal formed is carefully weighed.

Calculation.—Let

the wt. of the oxide taken $= w$ gms.

wt. of metal formed $= w_1$,,

Hence, the wt. of Oxygen $= w - w_1$ gms.

$$\therefore \text{ the Eq. wt. of the metal} = \frac{w_1}{w - w_1} \times 8$$

The equivalent weight of **copper** and **iron** may be determined by this method.

4. Conversion of the metal into its chloride.—A weighed quantity of the metal is converted completely into its chloride either by the direct action of chlorine or indirectly by first dissolving the metal in nitric acid and then precipitating the chloride if insoluble in water by hydrochloric acid. The precipitated chloride of the metal is washed, dried and carefully weighed.

Direct : Metal + Chlorine = Chloride of the metal

Indirect : $\text{Metal} \xrightarrow{HNO_3} \text{Nitrate of the metal} \xrightarrow{HCl} \text{Chloride of the metal}$

Calculation—Let

wt. of the metal taken = w gms.

wt. of the chloride formed = w_1 ,,

$\therefore$ wt. of chlorine = $w_1 - w$,,

Hence, the Eq. wt. of the metal = $\frac{w}{w_1 - w} \times 35{\cdot}46$.

The indirect method is used in determining the Eq. wt. of **silver.**

Eq. Wt. of Silver.—Weigh a piece of *clean* and *pure* Silver and dissolve it completely in dil. HNO_3 so that the sol. is *slightly acidic.* Heat the sol. to boiling and precipitate the whole of Silver by the addition of pure dil. HCl, drop by drop, until no more ppt. is formed. Allow the ppt. to settle. Filter it using a *tared* filter-paper, and wash the residue first with distilled water containing a little HNO_3 and then with water to remove HNO_3. Dry the ppt. at 100°C and finally at 130°C, in an air-oven. Now weigh it in a weighing tube. Repeat the processes of heating, cooling and weighing till the final weight is constant.

Calculation.—Let the wt. of Ag taken = a gms.

wt. of AgCl formed = b gms.

$\therefore$ wt. of Chlorine = $(b - a)$ gms.

Hence, the Eq. wt. of Silver = $\frac{35{\cdot}46 \times a}{(b - a)}$.

5. By double decomposition : Eq. Wt. of Sodium.—A weighed quantity of pure and dry sodium chloride is dissolved in distilled water and then silver nitrate solution is added till the precipitation of silver chloride is complete.

$$NaCl + AgNO_3 = \downarrow AgCl + NaNO_3$$

The ppt. is filtered, washed, dried and weighed.

Calculation—Let

wt. of NaCl taken = w gms.

wt. of AgCl formed = w_1 ,,

Now let the Eq. wt. of Sodium be x. Then, the Eq. wt. of NaCl $= x + 35{\cdot}46$.

Again Eq. wt. of AgCl $= 107{\cdot}88 + 35{\cdot}46$
$= 143{\cdot}34$.

(Equivalent of a compound is the sum of the equivalents of its constituent elements.)

$$\therefore \quad \frac{x + 35{\cdot}46}{143{\cdot}34} = \frac{w}{w_1}$$

Or, $x =$ Eq. wt. of Sodium

$$= \frac{w}{w_1} \times 143{\cdot}34 - 35{\cdot}46$$

The Eq. wt. of Potassium is determined in the same way.

Eq. Wt. of Non-metals

1. **Conversion into oxide**--The Eq. wts. of (i) Hydrogen and (ii) Carbon are determined by this method.

(i) **Eq. Wt. of Hydrogen**.—Hydrogen gas, carefully purified and dried, is passed over a weighed quantity of heated dry copper oxide and the amount of water formed is absorbed in a series of drying tubes.

After the experiment, the copper oxide and the drying tubes are weighed.

Calculation.—Let

(1) The decrease in wt. of CuO $= w$ gms.

Then the wt. of Oxygen which has combined with Hydrogen to form water is w gms.

(2) the increase in wt. of drying tubes $= w_1$ gms.

Hence, the wt. of water formed $= w_1$ gms.

$\therefore$ the wt. of Hydrogen $= w_1 - w$ gms.

$$\therefore \text{ Eq. wt. of Hydrogen} = \frac{w_1 - w}{w} \times 8.$$

(ii) **Eq. Wt. of Carbon**.—A weighed quantity of pure carbon is burnt completely in a current of dry oxygen gas and the CO_2 gas formed is absorbed in bulbs containing strong solution of KOH (Potash bulbs).

Calculation.—Let

wt. of Carbon $= w$ gms.

Increase in the wt. of potash bulbs $= w_1$ gms.
$=$ wt. of CO_2 formed.

Hence, the wt. of Oxygen $= w_1 - w$ gms.

$$\therefore \text{ Eq. wt. of Carbon} = \frac{w}{w_1 - w} \times 8.$$

Atomic and Molecular weights

Atomic weight.—No man has seen an atom even under the most powerful microscope and there is little chance that he ever will. To weigh this tiny mass of an atom in a balance is, of course, impossible. Scientists, very recently, however, have succeeded in obtaining the absolute weights of different kinds of atoms by indirect means. An atom of hydrogen has been found to weigh 0·000,000,000,000,000, 000, 000, 001, 673 gm. The absolute weights of atoms are so very small that it is not of much practical value for the day-to-day problems of chemistry. Long before the scientists were able to calculate the absolute weights of atoms, they devised a scale of atomic weights which was found to be more useful. It is based on the relative weights of different kinds of atoms compared to that of a standard element. Hydrogen being the lightest of all substances, it was at first chosen to be the standard element with 1 for its atomic weight.

The Atomic weight of an element is a number which expresses how many times the weight of one atom of the element is greater than the weight of one atom of Hydrogen.

$$\text{At. wt. of element} = \frac{\text{Wt. of 1 atom of the element}}{\text{Wt. of 1 atom of Hydrogen}}.$$

Thus the atomic weights are *not* the *actual* weights of atoms but the *relative* weights of the atoms of various elements expressed in terms of hydrogen taken as unit. Hence when we say that the atomic weight of chlorine is 35·46, we mean that an atom of Chlorine is 35·46 times heavier than an atom of hydrogen ; that is to say if the weight of one atom of hydrogen is taken as *unit*, the weight of 1 atom of chlorine will be 35·46 times the weight of 1 atom of hydrogen. Further, *if it were possible* to place 2 atoms of chlorine on the left-hand pan of a *very sensitive* balance, about 71 atoms of hydrogen would be required in the right-hand pan to counterpoise them.

From *a practical point of view*, it may also be defined thus—

The atomic weight of an element is the smallest weight of it present in the molecular weights of the compounds.

The gm. atomic wt. (or the **gram-atom**) of an element is its atomic weight expressed in grams. Thus 1 gm. atom of magnesium stands for 24 gms. of Mg.

The Oxygen Standard.—The hydrogen Standard of the At. wts. of elements, strongly advocated by Proust, had to be given up ; and at present, Oxygen with the value 16·000 has been accepted as the standard of At. wts. for the following reasons :—

(1) It is much easier to prepare compounds of elements (especially of metals) with Oxygen than with Hydrogen.

(2) Hydrogen being very light, experimental errors are more magnified when comparisons are made with it than with Oxygen.

(3) The At. wts. of elements do not come as near whole numbers when Hydrogen is taken as 1·000 as they do when Oxygen is taken as 16·000.

If the At. wt. of Hydrogen is taken as 1, then that of Oxygen is a little less than 16. Hence on the Oxygen standard ($O=16$), the At. wt. of Hydrogen is not 1, but a little more *i.e.*, 1·008.

Relation between Eq. Weights, Valency and Atomic Weight.

Let the At. wt. of the element be a and its eq. wt. and valency be e and v respectively.

Since the valency of the element is v, v atoms of Hydrogen combine with 1 atom of the element.

But the weight of v atoms of Hydrogen is $v \times 1·008$ and that of 1 atom of the element is a.

Hence, $v \times 1·008$ parts by wt. of Hydrogen combine with 'a' parts by wt. of the element.

Or, 1·008 parts by wt. of Hydrogen combine with $\frac{a}{v}$ parts by wt. of the element.

Hence, from the definition of equivalent weight,

$$\frac{a}{v}=e$$

$$\text{or,} \quad a=e\times v$$

i.e., **At. wt. = Eq. wt. × Valency.**

Determination of the Atomic Weight.

(1) Method based on the Eq. wts.—The valency of an element being a whole number, the At. wt. of an element is an exact multiple of its Eq. wt. As the Eq. wt. of an element can be determined with the highest degree of precision by one or other of the methods described in the previous chapter, the relation, At. wt. = Eq. wt. × Valency affords the most accurate method of determining the At. wts. of elements. The following is the outline of the method.

(i) Determine the Eq. wt. of the element *very carefully*.

(ii) Now determine an *approximate* At. wt. of the element by Dulong and Petit's Law (see P. 87) and thence work out the *valency* of the element, *which is always a whole number* ; and finally

(ii) Calculate the *exact* At. wt. of the element by multiplying the Eq. wt. of the element by the valency.

Illustration.—The Eq. wt. of Mg is found to be 12·16. Its approximate At. wt. determined by other methods, is 23.

∴ The valency of Mg is 23 ÷ 12·16 = 1·89. But the valency cannot be 1·89, a fractional number. It must be a whole number and we take it to be 2.

Hence, the *accurate* or *exact* At. wt. of Mg is 12·16 × 2 = 24·32.

(2) Method based upon the Specific Heats of *solid* **elements—Dulong and Petit's Law.**

This is a method of approximately determining the At. wts. of elements. It is applicable to the cases of solid elements only.

The French chemists Dulong and Petit in 1819 found out that the product of the Sp. heat of an element in the *solid* state and its At. wt. is constant, and is equal to 6·4. It is called Atomic heat.

Sp. heat × At. wt. = 6·4 (approx.)

Dulong and Petit's Law—The atomic heats of solid elements are the same, and are equal to 6·4. That is to say, the atoms of solid elements have the same capacities for heat energy.

Hence, the At. wt. = 6·4 ÷ Sp. heat.

N. B.—Dulong and Petit's Law holds true in the cases of solid elements only with the *exceptions of* **Carbon, Boron, Silicon,** *etc.*

(3) Method based upon Avogadro's Hypothesis (*Vapour density method*).—Atoms are indivisible. Therefore, the molecule of a compound of a particular element cannot contain less than one atom of this element. Consequently, the smallest wt. of the said element present in the Molecular wts. of a *large number* of its compounds will represent the At. wt. of the element. Hence, to determine the At. wt. of an element by this method—

(i) determine the Vapour densities of a *large number* of its *volatile* compounds,

(ii) calculate out their Mol. wts. from the relation—

Mol. wt. = 2 × density,

(ii) analyse each compound and determine the actual weight of the element present in the mol. wt. of each compound,

(iv) pick out the smallest wt. of the element present in the Mol. wts. of the compounds,

This smallest wt. will be the At. wt. of the element.

Illustration.

Atomic wt. of Nitrogen

Compound	Rel. density ($D_H=1$)	Mol. wt. = 2 × Rel. density	Wt. of Nitrogen in the Mol. wt. of the compound
Ammonia	8·5	17	14
Nitrous oxide	22·0	44	14 × 2
Nitric oxide	15·0	30	14
Nitrogen dioxide	28·0	46	14
Nitrogen trioxide	38·0	76	14 × 2

Therefore, 14 is the least weight of Nitrogen present in the Molecular weights of its various compounds. And since the atom of an element is the smallest particle of it which can enter into the composition of the molecule of its compounds, 14 *should* be the Atomic weight of Nitrogen.

N. B.—It will be observed from the above table that all the numbers in the last column are either 14 or *multiples* of 14. Therefore, unless all these compounds of Nitrogen contain more than one atom of Nitrogen, 14 being the *least wt* must be taken as the Atomic wt. of Nitrogen. We have considered a large number of compounds of Nitrogen, and it is quite *possible* that some of them will contain only *one atom* of Nitrogen. in the molecule. The result is that *for the present* we have no other alternative than to take the Atomic wt. of Nitrogen to be 14. If on any *future* date such a compound of Nitrogen is prepared or comes to exist, which contains less than 14 parts by wt. of Nitrogen in the Molecular wt. of that compound, 14 would *not then* be regarded as the Atomic wt. of Nitrogen.

There are several other methods of determining the At. weights of elements, but most of them like Dulong and Petit's method give only an approximate value of the At. wts. They are, as a matter of fact, methods for determining the valencies of elements *i.e.* the whole numbers by which their respective equivalent weights are to be multiplied to get the accurate values of their atomic weights.

Molecular weight.—The molecular weight of a substance is the sum of the weights of all the atoms present in one molecule of it. Thus the molecular weight (or formula weight) of sulphuric acid, H_2SO_4 is

$$\begin{array}{lll} H_2 = 1{\cdot}008 \times 2 & = 2{\cdot}016 \\ S = 32 \times 1 & = 32 \\ O_4 = 16 \times 4 & = 64 \\ \hline H_2SO_4 & = 98{\cdot}016 \end{array}$$

The present standard of molecular weights like that of atomic weights is an oxygen atom whose weight is taken to be 16.

The molecular weight of a substance is the weight of one molecule of the substance relative to the weight of one atom of oxygen taken to be 16.

Gram Molecular Weight (Gram-molecule).—The Gram Molecular Weight also called **gram-molecule** of an element or a compound is its molecular weight expressed in grams. Molecular Weight is a pure number, whereas gram molecular weight represents a particular weight of the substance. The Molecular weight of oxygen is 32 ; its gram molecular weight is 32 grams. Again, the molecular weight of carbon dioxide is 44 ; its gram molecular weight is 44 grams.

Again it has been shown as a corrolary of Avogadro's hypothesis that the gm. mol.-weights of all gases occupy 22·4 litres at N. T. P.

Hence the Mol. wt. of a substance may also be defined as a number which expresses in grams the weight of 22·4 litres at N. T. P. of the substance in the gaseous or vaporous state.

Determination of the Mol. weight.—

The Mol. wt. of a substance which is a gas or which can be vaporised without decomposition can be determined from its vapour density, for it has been already shown as a deduction of Avogadro's hypothesis that the Mol. wt. of a gas is two times its vapour density.

Several methods are known by which the vapour density of a substance can be determined of which Victor Meyer's method is the most important and generally used.

(1) Victor Meyer's Method.— This is a very simple and convenient method of determination of vapour-density.

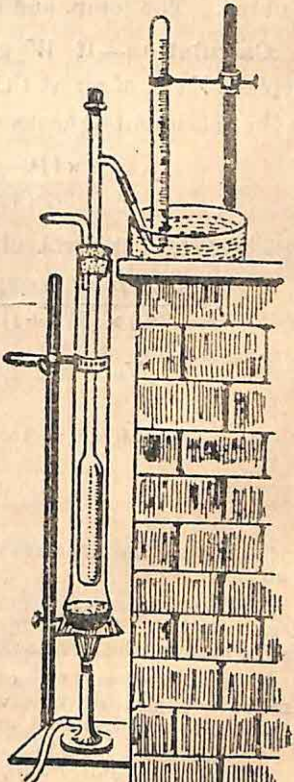


Fig. 29—Victor Meyer's Method.

The apparatus consists of a cylindrical glass vessel closed at the bottom and provided with a long neck and a side-tude. It is usually placed inside a *jacket*, or a *boiling-tube*, which ends in a bulb at the bottom. To start the experiment a liquid, whose boiling-point is 25° higher than the boiling-point of the substances whose vapour-density is being determined, is placed in the bulb of the jacket. The top of the inner cylindrical vessel is closed with a cork and the apparatus is placed inside the jacket. The liquid in the bulb is now heated to boiling. When the temp. of the whole apparatus has become steady and no more air from the inner tube comes out of the side-tube, the end of the side-tube is put under a gas-measuring tube filled with water and inverted over a trough of water. The cork is now withdrawn and a *weighed* quantity of the substance, enclosed in a small glass tube, is dropped into the inner vessel and the stopper is immediately replaced, care being taken to make it air-tight. The substance quickly vaporises and the vapours expel an **equal volume** of air which collects in the gas-measuring tube. When no more air issues from the side-tube, the gas measuring tube is closed with the thumb and is immeresd in a tall jar of water. After the gas has attained the temp. of water in the jar, the levels of water inside and outside are made the same, and the vol. of the displaced air is noted. The temp. and also the barometric pressure are noted.

Calculation—If W gms. of the substance on being vaporised, displace V c.c. of air at $t^\circ C$ and P mm. pressure, then taking f mm. to be the tension of aqueous vapour at t°, the vol. of air becomes,

$$\frac{V \times (P-f) \times 273}{760 \times (273+t)} \text{ c.c. at N. T. P.}$$

The Wt, of this vol. of hydrogen will be

$$\frac{V \times (P-f) \times 273}{760 \times (273+t)} \times {}^{\cdot}00009 \text{ gm.} = X \text{ gms.} \quad (\textit{suppose})$$

$$\therefore \text{ Vapour-density} = \frac{W}{X}$$

Hence, Mol, wt. $= 2 \times$ vapour density $= \dfrac{2W}{X}$

Exercise

1. What is the difference between the atomic weight and the molecular weight of an element? *Mad., 1931* : *Punj., 1912* ; *All., 1921.*

2. State Dulong and Petit's Law and explain its value on the determination of atomic weights. The chloride of a metal was found to contain 47·22% of the metal. Its Sp. heat is 0·094. What is its exact At. wt.? *Punj., 1926* ; *Bom., 1934.*

3. Explain clearly the connection between equivalent and atomic wts. 1 gm. of a metal evolves on treatmeat with a dil. mineral acid 34·2 c.c. of hydrogen at N. T. P. Calculate the equivalent wt. of the metal. What further information is required to determine its At. wt.? *Pat. Punj., 1923* ; *All., 1926* ; *C. U., Bom., 1919* ; **[Ans. = 32·48]**

4. If (i) common salt contains 60 p.c. of chlorine and (ii) assuming the specific heat of sodium to be 0·371, (iii) taking the equivalent wt. of chlorine to be 35·4 find the At. wt. and probable valency of sodium. **[Ans. At. wt. = 23·6 , Valency = 1]**

5. The specific heat of an element is 0·198. What is its probable atomic weight? *Nag., Pat., 1912.* **[Ans. = 32·32]**

6. 0·1 gm. of a certain metal when dissolved in dilute HCl, evolves 124·2 c.c. of hydrogen at N. T. P. The specific heat of the metal is 6·231. Find its equivalent wt., atomic wt. and valency. *C. U., 1953 ; All., 1939 ; Bom., 1916.*

[Ans. Eq. wt. =8·94 : At. wt. =26·23 , Valency=3]

7. In an experiment 0·49 gm. of a metal dissolved in HCl gave 295 c.c. of *dry* hydrogen at 22°C and 752 mm. The Sp. heat of the metal was 0·152. Calculate its chemical equivalent and the exact At. wt.

C. U., 1943. **[Ans Eq. wt' =20·15 ; At. wt. =40·3]**

8. The atomic weight of a metal is known to be roughly 70. What value would you expect for its sp. heat ? Give three possible values for its eq. wt.

[Ans. =0·00914 ; 70, 35 ; 23·3]

Define molecular weight of a substance and how it is determined ?

9. 0·3 gm. of a metal can produce 278·75 c.c. of dry Hydrogen at N. T. P. What is its chemical equivalent ? **[Ans. =12]**

10. 5 gms. of a metal liberate 0·0846 gm. of hydrogen from HCl and the same wt. of the metal yields 6·35 gms. of its oxide. Calculate the eq. wts. of the metal.

Banaras. 1930. **[Ans. =59·1 and 29·62]**

11. What is meant by equivalent weight of a metal ? 0·218 gm. of Mg gave 218·2 c.c. of *moist* hydrogen at 17°C and 754·5 mm. from HCl. Find the eq. wt. of the metal (tension of aqueous vapour at 17°C=14·4 mm.).

Bom., 1926 ; All., 1933. **[Ans. =12·24]**

12. 0·344 gm. of Tin combines with Oxygen to give 0·4365 gm. of SnO_2. What is the eq. wt. of Tin ? **[Ans. =29·7]**

13. 100 gms of Mg combine with 65·6 gms. of oxygen, 8 gms. of oxygen combine with 1 gm. of hydrogen. Find the equivalent wt. of magnesium.

London I. Sc. **[Ans. =12·19]**

14. The chloride of an element contains 38·11 per cent of chlorine. Find the equivalent wt. of the element. (Cl=35·46). *Bom., 1917.* **[Ans. =57·58]**

15. 0·5 gm. of Mg. displaces 0·041 gm. of hydrogen and 1·312 gms. of Cu. What are the eq. wts. of these elements ? **[Ans. =12·19 ; 31·986]**

16. 0·3 gm. of Zn displaces 1 gm. of Ag from $AgNO_3$ sol. What is the eq. wt. of Ag if that of Zn be 32·5 ? **[Ans. =108·3]**

17. 1 gm. of KCl solution gives 1·926 gms. of AgCl when treated with excess of $AgNO_3$ solution. Taking the eq. wt. of Ag as 108, that of Cl as 35·5, calculate the eq. wt. of potassium. *Lond., B. Sc.*

Let x be the eq. wt. of K. Then

$$\frac{x+35\cdot5}{108+35\cdot5}=\frac{1}{1\cdot926}. \quad \text{Or, } x=39\cdot006$$

18. Describe, in outline, two methods for the determination of the molecular weight of a gas. *Cal. Pre U. 1970*

19. What do you understand by statement—"The atomic weight of Chlorine is 35·5 ?.' *Cal. Pre-U. 1962.*

20. Explain with illustration the term ' Gram-molecule". *Cal. Pre-U. 1962.*

21. Explain the term "Equivalent Weight of an element" with illustration.

Cal. Pre. U. 1964.

22. What is meant by equivalent weight of an element ? Explain clearly the relation between the Equivalent Weight and Atomic Weight of an element.

0·05 gm of a metal when completely dissolved in hydrochloric acid, gave 51 c.c. of hydrogen measured dry at 27°C and 751 mm. pressure. Find the Equivalent weight of the metal. *Cal. Pre-U. 1966:* **[Ans: =12·1]**

CHAPTER XI

IONIC THEORY AND ELECTROLYSIS
FARADAY'S LAWS

Electric Current and Substances.—Substances behave differently towards the electric current : some allow current to pass freely through them ; others do not. This also true in the case of liquids. Some liquids like turpentine, petroleum, etc. do not allow current to pass through them. They are called **non-conductors.** Others like mercury, etc. allow current to pass freely through them. They are called **conductors.** The conductors again are divided into two classes :

(1) Conductors which undergo no change beyond becoming slightly warm by the passage of electricity through them. Metals are conductors of this type.

(2) Conductors which not only conduct electricity but get also decomposed during the passage of electric current. They are chiefly solutions of *acids*, *bases* and *salts*. These conductors are called **electrolytes.**

By **Electrolytes,** we, therefore, mean compounds which, in solution or in molten state conduct an electric current and get simultaneously decomposed by it. How they conduct electric current has been explained later (See ionisation and electrolytic dissociation below).

Electrolysis.—It means decomposing an electrolyte either in solution or in a fused state by passing electric current through it.

Electrodes.—The current is always *conveyed* to and *out of* an electrolyte by means of metal foils or plates or graphite poles kept immersed in it. They are called **electrodes.**

Anode (Gk. *ana=up* ; *hodes=path*) or the **Positive Electrode.**—It is the metal plate or foil or wire which is connected with the positive pole of the battery ; and, consequently, through it current **enters** the electrolyte.

Cathode (Gk. *kata=down* ; *hodos=path*) or the **Negative Electrode.**—It is the metal plate or foil or wire connected with the negative pole of the battery *i e.*, the one by which the current **leaves** the electrolyte.

The vessel in which electrolysis is carried out is often called an *Electrolytic Cell* or *Voltameter.*

Ionisation and electrolytic dissociation—When electricity is passed through water which has been acidified with a few drops of sulphuric acid, we find that hydrogen is set free at the cathode and oxygen at the anode. In the same way, by the electrolysis of copper chloride we get copper at the cathode and chlorine at the anode.

The results obtained from the electrolysis of the above solutions lead us to the conclusion that the **Metals** and **Hydrogen** are liberated at the **cathode**, while the **Non-metallic portion** of the electrolyte is liberated at the **anode** Now, the hydrogen or the metallic portion of the electrolyte is supposed to be *attracted towards* the negative electrode before liberation at it. This attraction can only be possible if the hydrogen or the metallic portion be charged with positive electricity. Similar is the case with the non-metallic portion, which must be charged with negative electricity.

The portion charged with positive electricity and which is liberated at the negative electrode (*i.e.*, *cathode*) is called the **positive ion or cation**; and that charged with negative electricity and which is liberated at the positive electrode (*i.e.*, *anode*) is called the **negative ion and anion.** This breaking-up of electrolytes in solution into ions is known as **electrolytic dissociation** which is a special case of **ionisation.** Ionisation and electrolytic dissociation are often used synonymously, though really there is a well-defined difference between the two terms. Ionisation has a wider meaning which includes all processes in which ions are formed. For example, the formation of ions of a gas, (neon) by a high tension current is also referred to as ionisation.

Thus we see that **metals** are all **electro-positive** in character; while **non-metals** are all **electro-negative** in character. Hydrogen, though a non-metal is electro-positive.

Ion.—An ion is an atom or a group of atoms (*i.e.*, *radicals*) **carrying positive or negative charge of electricity.** It is usually formed by the dissociation of an electrolyte in aqueous solution. The process is called ionisation. It is reversible.

The Ionic Theory or the Theory of Electrolytic Dissociation.

Arrhenius' Ionic Theory may be *briefly* stated thus :—(i) When an electrolyte (*i.e.*, an acid, a base, or a salt) is dissolved in water (or in other *ionising* solvents), a molecule of the electrolyte which is electrically neutral, breaks up into two or more ions of two different kinds; the amount of *positive* charge on one kind being *exactly equal* to the amount of *negative* charge on the other. The ions produced exist in equilibrium with the undissociated molecules. Thus

$NaCl \rightleftharpoons Na^+ + Cl^-$ | $NaOH \rightleftharpoons Na^+ + (OH)^-$

Again, this breaking-up of the electrolytes in solution *may not* be complete in all cases. It *may* happen that ions carrying the same amount of the *different* kinds of electricity are attracted towards each other, with the result that the positive charge neutralizes the negative charge and the original molecules are reformed. (fig. 30).

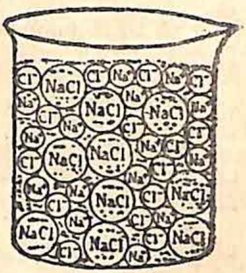


Fig. 30—Ionic Dissociation of NaCl in solution

There takes place, therefore, a kind of dissociation (i.e., *breaking-up* and *re-union*) inside the solution. Such a dissociation, resulting in the formation of ions in solution, is called **Ionic or Electrolytic dissociation** (Ion, from Gk. *Iwo* = traveller). (ii) The dissociation increases with dilution, and at infinite dilution, the electrolyte is said to completely break up into ions.

Unlike acids, bases and salts, most organic compounds such as cane sugar, glucose, alcohol etc. do not yield ions in solution. They are, therefore, non-electrolytes and hence, their solutions *do not conduct electric current.*

(iii) It is the ions, and *not* the undissociated molecule, which conduct electricity. The *anions* and *cations* migrate towards the *anodes* and *cathodes* respectively and are discharged there. Also the liberation of the ions at the electrodes depends upon their *discharge potentials*. That is to say, the ions which require the minimum E.M.F. for their discharge at the electrode and get converted into neutral atoms or radicals, will be liberated *first* and then the other ions *in the said order*.

Ions and Atoms.—When NaCl is dissolved in water it breaks up (*i.e., ionises*) into Na-ions and Cl-ions. Now the question is—"How is it that sodium-ion does not react with water and give NaOH ?" The question is answered by saying that as soon as sodium atom is changed into sodium-ion by being charged with *one unit of positive* electricity, its ordinary chemical properties are changed ; and consequently it does not decompose water until it is again discharged.

Electrolysis explained in the light of Ionic Theory

(1) *Electrolysis of molten sodium chloride.*—Let us take some sodium

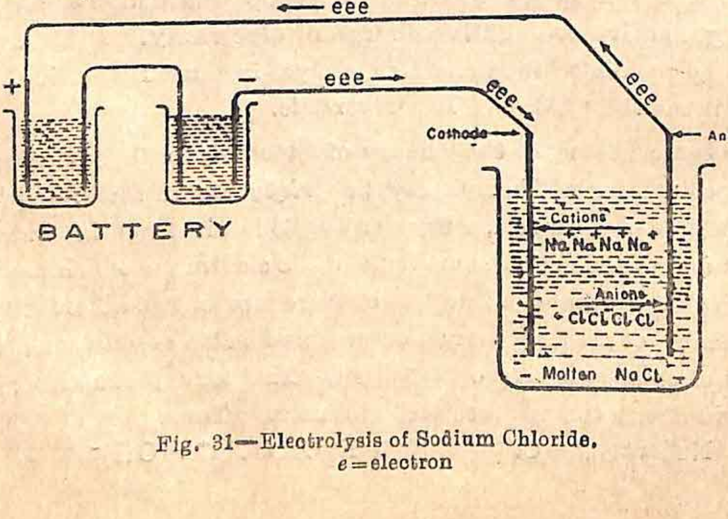


Fig. 31—Electrolysis of Sodium Chloride.
e = electron

chloride and melt it down in a vessel. Molten sodium chloride is a good conductor of electricity. Now let us put two electrodes into the molten bath of sodium chloride and connect the electrodes to a battery. One of the electrodes is made the positive and the other the negative. A battery or a dyanamo does not generate electrons, but only acts as a pump circulating electrons between the anode and the cathode. According to the ionic theory, sodium chloride in the molten state is ionised into Na^+ ions and Cl^- ions. When electric current is passed, Na^+ ions because of their positive charge move towards the cathode which is the negative electrode and Cl^- ions due to their negative charge move towards the anode which is the positive electrode. On reaching the cathode, each Na^+ ion receives an electron from the cathode and is immediately discharged as a neutral atom. (fig. 31)

$$Na^+ + e = Na$$

$$\text{or,}\quad 2Na^+ + 2e = 2Na.$$

Similarly each Cl^- ion on reaching the anode is made to give up its electron which immediately pumped over by the battery to the cathode to replace the one removed by the Na^+ ion. The Cl^- ions on losing their extra electrons are converted into atoms of chlorine which pair up in twos to form molecules.

$$Cl^- = Cl + e$$

$$\text{or}\quad 2Cl^- = Cl_2 + 2e$$

The over-all equation may be written by combining the partial reactions.

$$\begin{array}{rl} 2Na^+Cl^- = & 2Na^+ + 2Cl^- \\ 2Na + 2e = & 2Na \\ 2Cl^- \quad = & Cl_2 + 2e \\ \hline 2Na^+Cl^- = & 2Na + Cl_2 \end{array}$$

(2) *Electrolysis of sodium chloride solution.*

When sodium chloride is dissolved in water, it ionises reversibly into Na^+ ions and Cl^- ions.

$$NaCl = Na^+ + Cl^-$$

The water is also slightly ionised giving rise to H^+ ions and OH^- ions.

So the solution contains four species of ions, namely Na^+ ions. Cl^- ions, H^+ ions and OH^- ions. When an electric current is passed through the solution by means of two carbon electrodes which form a part of an electrical circuit, the positive Na^+ and H^- ions move towards the cathode and the negative Cl^- and OH^- ions towards the anode.

At Cathode, H^+ ions have lower discharge potential which means that H^+ ions accept electrons more readily than Na^+ ions and hence the former ions are discharged preferentially *as* hydrogen atoms. Hydrogen atoms immediately combine in pairs to form molecules of hydrogen.

$$H^+ + e = H$$
$$H + H = H_2$$

At the anode similarly, Cl^- ions having lower discharge potential give up their electrons more readily than OH^- ions and hence are preferentially discharged as atoms which immediately pair up to form molecules

$$Cl^- = Cl + e$$
$$Cl + Cl = Cl_2$$

Therefore Na^+ and OH^- ions accumulate in solution and these are the component ions of caustic soda.

The over-all result is the production of H_2, Cl_2 and caustic soda.

$$2Na^+ Cl^- + 2H_2O = 2Na^+ OH^- + H_2 + Cl_2$$

(3) *Electrolysis of acidulated water.*

Water is a weak electrolyte. It ionises only to a small extent. $H_2O \rightleftharpoons H^+ + OH^-$. It is therefore a bad conductor of electricity. When, however, a few drops of sulphuric acid (or any other strong acid) are added to it, the solution contains a large number of H^+ ions due to almost complete ionisation of sulphuric acid.

$$H_2SO_4 = 2H^+ + SO_2^{--}$$

On now passing an electric current, H^+ ions move to cathode. where each H^+ ion on receiving an electron is discharged as a hydrogen atom. Two of the discharged atoms combine to form a molecule of hydrogen.

$$H^+ + e = H$$
$$H + H = H_2$$

Both SO_4^{--} and OH^- ions move to the anode where the OH^- ions are preferentially discharged losing their electrons. The discharged OH groups react amongst themselves to set free oxygen.

$$OH^- = OH + e$$
$$4OH = O_2 + 2H_2O$$

Thus on electrolysis of acidulated water, hydrogen evolves at the cathode and oxygen at the anode.

The Units : (1) Coulomb.—It is the *unit quantity of electricity.* A coulomb is defined as the quantity of electricity that liberates ·001118 gm. of silver or ·0000104 gm. of hydrogen.

It is *also defined as* the quantity of electricity that passes through a circuit when a current of *one ampere* strength is passed through the circuit for *one second.*

$$\text{Coulomb} = \text{Ampere} \times \text{Second}.$$

(2) **Faraday.**—This is *also* taken as the unit quantity of electricity, and may be called the 'bigger unit' just as metre is a bigger unit, while centimetre is a small unit.

1 Faraday = 96,540 coulombs. Now, 1 coulomb liberates ·001118 gm. of Ag.

∴ 96,540 coulombs will liberate (96,540 × ·001118) = 108 gms. of Ag.

Hence, 1 Faraday is the quantity of electricity required to liberate 1 gram-equivalent of Ag or any other element (—2nd Law of Faraday).

Faraday's Laws of Electrolysis.

First Law.—*The mass of an ion, liberated during electrolysis, is directly proportional to the quantity of electricity which has passed through the electrolytic cell.*

It follows from the 1st law that if W be the mass in gm. of ion liberated ; C, the strength of current in ampere ; t, the time in second ; and Q, the quantity of electricity in coulomb, then—

$$W \propto Q. \quad \text{But } Q = C \times t.$$

$$\therefore \; W \propto C \times t$$

$$\text{Or, } \; W = Z \times C \times t, \text{ where } Z \text{ is a constant.}$$

Now, If $Q=1$ (*i. e.* $C=1$, and $t=1$), $Z = W =$ *mass of ion liberated by unit quantity of electricity.* This is called the *electro-chemical equivalent* of the substance and is written as E. C. E.

Electro-chemical Equivalent of elements.—*The mass in gms. of an element which is liberated by the passage of unit quantity, viz. 1 coulomb of electricity, is called the electro-chemical equivalent of the element.*

Second law.—*When the same quantity of electricity is passed through different electrolytes, the relative masses of ions liberated are proportional to their chemical equivalents.*

The Second Law states that if the same quantity of electricity is passed through a number of cells, connected in series and containing say Na_2SO_4, $CuSO_4$, $AgNO_3$, $Zn(NO_3)_2$ sol. respectively, then the relative amounts of the elements liberated will be proportional to their equivalent weights.

That is to say, when 1·008 gms. of H are liberated in one cell, there will be liberated 8 gms. of O, 63·5 ÷ 2 gms. of Cu, 108 gms. of Ag, 197 ÷ 3 gms. of Au and 65 ÷ 2 gms. of Zn in the other cells.

From the 2nd Law it follows that the electro-chemical equivalent (E. C. E) of an element is directly proportional to its chemical equivalent. Thus

$$\frac{\text{E. C. E. of an Element A}}{\text{E. C. E. of an Element B}}=\frac{\text{C. E. of A}}{\text{C. E. of B}}.$$

Similarly, $$\frac{\text{E. C. E. of any Element}}{\text{E. C. E. of Hydrogen}}=\frac{\text{C. E. of the Element}}{\text{C. E. of H.}}$$

$$=\text{C. E. of the element } (\because \text{ C. E. of H}=1).$$

N. B.—The value of the E. C. E. of an element depends upon the unit we choose. If *coulomb* be taken as the unit, E. C. E. of H is ·0000104 gm.

E. C. E. of an element = Its C. E. × ·0000104 gm.

Problems.

1. *Find the wt. of Cu deposited from $CuSO_4$ sol. by a current of 0·25 amp. flowing for 1 hour.*

$Q=C\times t=0{\cdot}25\times 60\times 60=900$ coulmbs.

96,540 coulombs liberate 31·5 gms. of Cu. ∴ 900 coulombs will liberate $(900\times 31{\cdot}5)\div 96{,}540=0{\cdot}293$ gm. of Copper.

2. *If 3 amp. current deposit 4 gms. of Ag in 20 minutes, what is the E. C. E. of Ag?*

$W=CZt$. Or, $Z=W\div Ct=4\div(3\times 20\times 60)=0{\cdot}0011$ gm.

3. *Current is passed through two cells connected in series containing acidulated water and lead acetate solution respectively. What wt. of Pb will be deposited when ·05 gm. of H_2 is evolved?*

Eq. wt. of $Pb=207\div 2=103{\cdot}5$.

Wt. of Pb liberated ÷ Wt. of H liberated = Eq. Wt. of Pb ÷ Eq. Wt. of H. Hence, Wt. of Pb liberated $=\dfrac{103{\cdot}5\times{\cdot}05}{1{\cdot}008}=5{\cdot}134$ gms.

Definitions of Acids, Alkalis and Salts in the Light of the Ionic Theory—

(1) An *acid* is a substance which in solution in water ionises giving H-ions, and no other *positively* charged ions. (2) An *alkali* is a substance which in aqueous solution ionises giving (OH)-ions and no other *negatively* charged ions. (3) A *salt* is a substance which in aqueous solution gives neither H-ions nor (OH)-ions as *primary products*.

Strength of Acids.—It depends upon the number of H ions given by different acids in equivalent solutions, that acid being the strongest which gives the largest number of H-ions under like conditions. The mineral acids are stronger than the organic acids. HCl is the strongest of all acids, stronger than HNO_3, H_2SO_4, etc.

Strength of Alkalis.—It depends upon the number of (OH)-ions given by different alkalis in equivalent solutions. KOH is a very strong alkali. $NH_4(OH)$ is a weak alkali.

From the *electronic point of view*, an acid is a *proton donor*; while a base is a *proton acceptor*.

According to the latest theory a H^+ unit does not exist as such in solution but combines with a molecule of water to form a hydronium ion,

$$H^+ + H_2O = H_3{}^+O$$

$$HCl + H_2O = H_3{}^+O + Cl^-.$$

Hydronium ion

This explains the part played by the solvent in the ionisation of an electrolyte.

Chemical reactions between electrolytes and ionic theory.

A beginner in chemistry is apt to make the mistake of thinking that a chemical reaction should occur because an equation for it can be written. It is not always true, for example, the equation, $KNO_3 + NaCl = KCl + NaNO_3$ has no meaning at all. According to ionic theory, electrolytes are ionised in solution and they should be written in ionic forms. The above equation in ionic form is therefore,

$$K^+ + NO_3{}^- + Na^+ + Cl^-$$
$$= K^+ + Cl^- + Na^+ + NO_3{}^-$$

This means that no change has taken place beyond the mixing of ions.

A chemical reaction may take place between electrolytes if one of the following conditions is fulfilled.

(1) The mixture of the electrolytes in solution contains a pair of ions which may give rise to an insoluble solid by their combination. Thus in the above reaction, if silver nitrate is substituted for potassium nitrate, then a reaction does take place with the separation of insoluble silver chloride.

$$Ag^+ + NO_3{}^- + Na^+ + Cl^-$$
$$= \downarrow AgCl + Na^+ + NO_3{}^-.$$

(2) If any pair of ions gives rise to an insoluble gas,

$$2Na^+ + CO_3{}^{--} + 2H^+ + 2Cl^-$$
$$= 2Na^+ + 2Cl^- + H_2O + \uparrow CO_2 \text{ gas}$$

(3) If any pair of ions produces a weekly ionised substance even if the products are soluble in water.

$$Na^+ + OH^- + H^+ + Cl^-$$
$$= Na^+ + Cl^- + H_2O.$$

Here one of the products, namely water is weakly ionised and hence, the reaction takes place although the products are all soluble in water. Ionic reactions take place with comparative ease almost instantaneously when the reactants in the form of solutions are brought together. Covalent compounds do not ionise in solution. It is much more difficult to bring about reactions between organic compounds which are mostly covalent.

Practical Application of Electrolysis.

1. *In Electro-plating and in Electrotyping.*

Electroplating means the deposition of a layer of metal, usually thin on a metallic object by electrolysis. The object is made the cathode in an electrolytic bath containing a solution of a salt of the metal to be deposited, the anode also consisting of the same metal. The purpose of electroplating is usually to afford protection against corrosion and/or to decorate. Also by suitable procedure, shapes or forms such as those of printed types or of any other object are reproduced by electrolysis, when the process is known as electro-typing (See under Ag, Ni etc.)

2. *In extraction of metals from their ores by means of electric current.*

(See extraction of Na, Al, Cu, Mg.)

3. *In electro-refining of metals.* (See Cu, Ag etc.)

4. *In the manufacture of chlorine, potassium chlorate, caustic soda, oxygen, hydrogen, etc.*

5. *In quantitative Chemical Analysis.*

Exercise.

1. What do you mean by ions, electroplating, cathode, anode, and coulomb ?
Punj., 1932 ; C. U., 1932, '38.

State Faraday's laws of electrolysis. What is the relation (*a*) between the electro-chemical equivalent of an element and its chemical equivalent, and (*b*) between the At. wt. and the Eq. wt. ? Calculate the electro-chemical equivalents of Ag and oxygen, given the E. C. E. of H=0·0000104, At. wt. of Ag=108, At. wt. of O=16.

2. What is the electro-chemical equivalent of an element ? Assuming the E. C. E. of Ag to be 0·001118, find the E.C.E. of oxygen (Ag=108.)
Bom., 1931 ; All , 1925 ; C. U., 1936, '43, '45.
C. U. 1932, '34, '38, '49. [**Ans. = ·0000828**]

3. State Faraday's laws of electrolysis. What current strength in ampere will be required to liberate 10 gms. of Iodine from KI sol in one hour ?
All., 1933. [**Ans. = 21 amperes**]

4. How many coulombs of electricity would be required to deposit 1000 gms. of Cu from a copper salt sol. ? Cu=63·5. [**Ans. = 3028919 coulombs**]

5. A current of 0·5 ampere strength passing through $AgNO_3$ sol. for 6 minutes deposits 2014 gm. of Ag. What is the E.C.E. of Ag ? [**Ans. = 0·001118**]

6. How much Zn will be consumed in a battery of 5 cells, when the current has liberated 0·05 gm. of H in a water voltameter ? [**Ans. = 5 × 1·625 gms.**]

7. How long will it take 5 ampere current to deposit 2 gms. of copper ?
[**Ans. = 20 mts. 13 secs.**]

8. What is meant by the term electrolysis. Describe the preparation of any compound where electrolysis is employed, *Cal. Pre U. 1970*

9. Calculate the E.C.E. of Ag, Cu and O, given the E.C.E. of H=0·0000104 and the At. wt. of Ag=108 C.E. of Cu=31·75 and C.E. of O=8.
C. U. 1936. [**Ans. Ag=0·0011232., Cu=0·0003302 ; O=0·0000832**]

10. Write a clear account of the Ionic Theory. What wt. of Ag will be deposited by 2·1 amp. current flowing for 20 minutes through $AgNO_3$ sol. ?
All., 1915 ; Panj. 1927 ; Banaras, 1933 ; Nag. 1233. [**Ans. = 1·817 gms.**]

11. State the laws of electrolysis. The same current is passed through acidulated water and $SnCl_2$ sol. What volume of dry detonating gas at N.T.P. is evolved from water when 1 gm. of tin is deposited from the other solution ?
Lond. I. Sc. ; C. U., 1936, '49. [**Ans. = 282 c. c.**]

12. A solution of a salt of a metal of At. wt. 112 was electrolysed for 12 minutes with a current of 1·5 amperes. The wt. of the metal deposited was 0·783 gm. Find the valency of the metal in the salt. *Lond. B. Com.*

13. An electric current is passed simultaneously through—(*a*) acidulated water (*b*) $CuSO_4$ sol. and (*c*) $AgNO_3$ sol. What substance and how many grams of each are liberated in each cell in the time that 124·7 c.c. of hydrogen at 27°C and 740 mm. are liberated ? *New Zealand Uni. : Bom., Eng., 1919*

14. The Cu-anode of a cell containing $AgNO_3$ sol. weighs 60 gms. After passing current for some time, it is found that 3·13 gms. of Ag are deposited on Pt. cathode. What is the final wt. of the anode ? ($Cu=63·5$) **[Ans.=59·08 gms.]**

15. Write short notes :—(*a*) Faraday's Laws of Electrolysis, (*b*) Ionic Dissociation. *Cal. Pre-U. 1961, '64.*

16. Explain the following terms with illustrations :—

(*a*) Electrolysis.

(*b*) Dissociation. *Cal. Pre-U. 1962.*

17. Explain the term 'Ion' with illustration. *Cal. Pre-U. 1963.*

18. A solution of sodium chloride can conduct electric current but a solution of Cane Sugar cannot. Explain this anomaly. State and explain Faraday's Laws of Electrolysis.

The weight of Copper deposited from a solution of Copper Sulphate by a uniform current 0·25 ampere flowing for one hour is 0·295 gm. Find the equivalent weight of Copper. (1 Faraday=96500 Coulombs) *Cal. Pre-U. 1966.* [Ans.=31·6]

19. Explain and illustrate :

Chemical equivalent and electrochemical equivalent. *Cal. Pre-U. 1967.*

CHAPTER XII

THE CLASSIFICATION OF THE ELEMENTS

Periodic Law

History.—As early as 1817 Dobereiner pointed out that the atomic weight of the middle member of a group of three correlated elements was a mean between the At. wts. of the first and the last. These are known as **Dobereiner's triads :**

Ca . . 40	Cl . . 35	Li . . 7
Sr . . 87	Br . . 80	Na . . 23
Ba . . 137	I . . 127	K . . 39

In 1868 Newland enunciated his **Law of Octaves** thus :—When the elements are arranged in the increasing order of their *atomic* wts. *the eight elements—starting from a given element—is a kind of repetition of the first, like the eight note in an octave of the music.*

Possibly on account of faulty atomic wts., then known, the law of octaves did not receive the attention it deserved.

PERIODIC TABLE

(with Atomic number written *above* and Atomic weights written *by the side of* the symbols)

Periods	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII	Group 0
	R_2O RH A B	R_2O_3 RH_2 A B	R_2O_3 RH_3 A B	R_2O_4 RH_4 A B	R_2O_5 RH_5 A B	R_2O_6 RH_2 A B	R_2O_7 RH A B	R_3O_8→*forml. of oxides* →*forml. of hydride.* A	*Or* Gr. VIII B
1							1 H 1·008		2 He 4
2	3 Li 6·94	4 Be 9·02	5 B 10 82	6 C 12	7 N 14·01	8 O 16	9 F 19		10 Ne 20
3	11 Na 23	12 Mg 24·3	13 Al 26·97	14 Si 28·06	15 P 31·04	16 S 32	17 Cl 35·46		18 A 39·9
4	19 K 39·1 29 Cu 63 5	20 Ca 40 30 Zn 65·3	21 Sc 45·1 31 Ga 70	22 Ti 48·1 32 Ge 72·5	23 V 51 33 As 74·9	24 Cr 52 34 Se 79·2	25 Mn 54·9 35 Br 79 9	26 27 28 Fe 55·8 Co 58·9 Ni 58·6	36 Kr 83·7
5	37 Rb 85·4 47 Ag 107·8	38 Sr 87·63 48 Cd 112	39 Y 88·9 49 In 114·8	40 Zr 91·20 50 Sn 119	41 Nb 92·9 51 Sb 121·76	42 Mo 46 52 Te 127·6	43 Tc 99 53 I 126·9	44 45 46 Ru 101·7 Rh 103 Pd 106	54 Xe 131
6	55 Cs 132·9 79 Au 197·2	56 Ba 137·37 80 Hg 200·6	57 La 139 *58—71 Rareearths 81 Tl 204	72 Hf 178·6 82 Pb 207·2	73 Ta 180·8 83 Bi 209	74 W 184 84 Po 210	75 Rs 186·3 85 At 210	76 77 78 Os 191 Ir 193 Pt. 195	86 Rn 222
7	87 Fr 223·1	88 Ra 226	89 Ac 227	90 Th 232·12	91 Pa 231	92 U 238·14			

* Rare earths.—58 59 60 61 62 63 64 65 66 67 68 69 70 71
Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tu, Yb, Lu.

N. B. Transuranium elements are not included in the table.

In 1869, the Russian chemist Mendeleeff, and in 1870, the German chemist Lother Meyer, quite independent of each other, discovered that *when the elements are arranged in the order of increasing atomic wts., their properties vary from member to member in a definite way, but return more or less to the same value at fixed points in the series.*

The Periodic Law.—The physical and chemical properties of the elements and their compounds are periodic functions of their atomic weights.

It means that the properties of the elements and their compounds vary after regular interval with variations in the atomic wts. That is to say, the properties go on changing as the atomic wts. go on increasing. Now, after *regular intervals*, the properties are repeated although the atomic wts. *still go on increasing.* Thus the properties *are periodic functions of the atomic wts.*

The Periodic Table.—Mendeleeff arranged the elements in a table called the *periodic table* or *periodic system.* The original table, however, has undergone many modifications with the discovery of new data. Such a modified table is given in page No. 102.

Main Features of Mendeleeff's Periodic Classification.

Study and Explanation of the Table.—In the table the elements are arranged **in the order** of their **increasing atomic weights** in horizontal series, in such a way that elements having similar properties are placed in the same vertical column. The horizontal series are generally written as **periods**, and the *nine* vertical columns, headed by the Roman numbers from I to VIII and Zero (0), are called **groups** The periods are **short** or **long.**

Short and Long periods. *Period 1.*—It consists of the two elements H and He.

Period 2.—Lithium forms the starting-point of the following series of 8 elements :—

Li Be B C N O F Ne

in which there is a regular change from the strongly electropositive element Li to the strongly electro-negative element F which is followed by the *inert* element Ne.

Period 3. After Neon, comes sodium which forms the starting-point of another series of 8 elements.

Na Mg Al Si P S Cl A

in which Na resembles Li, Mg resembles Be, Al resembles B ; and so on. Such periods of 8 elements are called **short periods** (—*Lowry*).

Thus the periodicity of properties of the 2nd period occurs again in the 3rd period.

Period 4.—The fourth period begins with potassium which strongly resembles sodium, but in this case we have to pass over 18 elements *instead* of 8, before another element rubidium strongly resembling potassium, is reached. Such a period of 18 elements is called a **long period.**

Period 5.—Starting again from Rb an identical sequence is met with.

Period 6.—The sixth period consists of 32 elements and is, therefore, called a *very long* period, or a *monster period.*

Period 7.—The seventh period is fragmentary. It starts like a long period, but soon comes to an end. Uranium, occupying the 4th place, is the element of the highest known atomic wt. occuring in nature. Several man-made elements (transuranium elements) have been prepared in recent years having At. wts. even higher than that of uranium.

Intervals of Periodicity.—Thus we see that the intervals of Periodicity are 8, 18, 32,......or twice the squares of 2, 3, 4, *taken in order*.

Odd series—The last *seven* elements of a long period form the *odd series.*

Group Zero.—The inert gases like helium, argon, etc. present in the air were discovered afterwards. They are placed in Zero group. They being inert and having no valency, stand between the highly electro-positive alkali metals and the strongly electro-negative halogens.

Sub-groups.—Each group is divided into *sub-groups A* and *B.* The elements belonging to the even series of their respective long periods are placed to the left (*sub-group A*), while those belonging to the odd series are arranged on the right-hand side (*sub-group B*) of each vertical column. The members belonging to a sub-group are *more closely* related than the other members of the same group.

The Rare Earths.—Lanthanum in Group III and in the 6th period, forms a cluster with fourteen other elements (At. nos. 58—71) which have got atomic weights differing by one or two, or four ; they are analogous in chemical properties, and it is very difficult to separate them in analysis. They are known as the elements of the *rare earths.*

The Radio-active elements.—There is also a class of elements, constituting the *last period of the table*, which differ from the rest in-as much as they are *radio-active i.e.*, they constantly liberate energy which appears to be derived from the disintegration of atoms.

Periodicity in the properties of the elements, when arranged in the Periodic Table, is shown by :

1. **Valency.**—The valencies towards *hydrogen* regularly *increase* up to the middle of a short period and then gradually *fall* and come back to unity. The valencies towards *oxygen*, on the other hand, increase regularly from 1 to 8, end there and begin from 1 again. Elements of Gr. 0 have no valency.

2. **Electro-chemical Character.**—In Gr. I we find the elements which are highly *electro-positive* (strongly basic). Coming to the middle, we find electrically indifferent elements like C, Si, etc. Further on, we find the highly *electro-negative* elements (strongly acidic), *viz.* the halogens.

3. **Other properties.**—The same periodicity in the properties can be observed with regard to the

(*a*) Melting-point, (*c*) Specific gravity,
(*b*) Boiling-point, (*d*) Atomic volume, etc.

N. B.—The only physical property which is *not periodic* is the atomic heat at the ordinary temps. although at low temps. it is *periodic*.

4. *Lastly*, there is a *regular gradation* in the properties of the elements belonging to the same group.

Application of the Periodic Law.—The periodic law has found application in three ways :—

1. **In Classification of Elements**—Of the various methods of classifying the elements, the periodic system is considered to be the best. It has reduced the study of the chemistry of one hundred elements practically to that of nine Groups only. The result is that—

(*a*) We can form an idea of the properties of an element and its compounds by knowing the Group it belongs to ; and

(*b*) We can compare the properties of different elements and their compounds belonging to different groups.

2. **In the Prediction of New Elements.**—When Mendeleeff first prepared the periodic table many *blank spaces* were automatically left in it. For example, the places where scandium, gallium, and germanium now stand, were then left blank. And by studying the properties of the elements surrounding the said blank spaces, Mendeleeff took the very bold step of predicting the properties of these unknown elements which he named as—

eka-boron, *eka*-aluminium and *eka*-silicon.

It is interesting to note how the prediction of the great scientist came to be fulfilled. The table below contains the *predicted* and *observed* properties of *germanium* which was discovered 15 years *after* Mendeleeff's prediction.

Properties of eka-silicon predicted by Mendeleeff in 1571	*Properties of germanium discovered by Winkler in 1886*
At. wt. =72	At. wt. =72·6
Sp. gr. =5·5	Sp. gr. =4·37
At. vol. =13	At. vol. =13·2
Dirty grey in colour.	Greyish-white in colour.
Should give a white oxide (RO_2) on ignition.	Gives a white oxide (GeO_2) on ignition.
Action of acids would be *slight*.	The metal is not attacked by HCl. It dissolves in *aqua regia*.
Action of Alkalis would be more marked.	Solution of alkalis have no action on the metal. *Fused* KOH or NaOH oxidizes Ge with incandescence.
The oxides would be refractory; the sp. gr. would be 4·7. The oxide would be feebly basic.	GeO_4 is refractory: the sp. gr. is 4·703. It is very feebly basic.
The chloride would be a liquid.	$GeCl_4$ is a liquid.
The fluoride would *not* be gaseous.	$GeF_4, 3H_2O$ is a white. crystalline solid.

The discovery of scandium and gallium *also* fulfilled Mendeleeff's prediction about *eka*-boron and *eka*-aluminium respectively.

3. In Correcting Doubtful Atomic Weights.—An element has got *only one* proper place in the Periodic table. That place may be fixed by comparing its properties with those of the neighbouring elements. In determining the atomic wt. of an element, if ever difficulty arises as to which multiple of its Eq. wt. is to be taken, we can easily decide it by finding out the proper position of the element in the table.

Defects of and misfits in the periodic system.—The periodic classification is not free from defects and apparent contradictions. The following are the defects of the system :—

1. A suitable location has not been found for the rare-earth elements.

2. Some of the elements having higher atomic wts. have been placed before elements of lower atomic wts. e.g.—

(*a*)	**Argon**	(39·9)	goes before	**Potassium**	(39·1)
(*b*)	**Cobalt**	(59·9)	,, ,,	**Nickel**	(58·6)
(*c*)	**Tellurium**	(127·6)	,, ,,	**Iodine**	(126·9)
(*d*)	**Protoactinium**	(231)	,, ,,	**Thorium**	(232·1)

N. B. This defect disappears if the elements are arranged in the order of their *Atomic Numbers* which are fundamental properties of the elements.

As the atomic numbers of A, Co, Te, Pr are *less* than those of K, Ni, I, Th respectively the former must, as they do, go before the latter. The arrangement now is that each element has been allocated a seat in the table from 1 onward, depending upon the net positive charge in its nucleus. Thus the lightest element H with one positive charge occupies the first, helium with two the second, lithium with three the third seat and so on.

Hence, the Periodic Law states :—**The properties of the elements are periodic functions of their Atomic Numbers.**

3. **The periodic arrangement overlooks some chemical analogies.** (*a*) *Some chemically dissimilar elements have been placed in the same group.* Thus,

Copper, silver and gold having very little analogies with sodium, potassium, lithium etc. have been placed in the same group with the alkali metals. Similarly, manganese has been placed in the same group with the halogens.

(*b*) *Some chemically similar elements have been placed in separate groups.* Thus,

Copper and mercury, silver and thallium, barium and lead, which appear to be chemically similar, have been placed in separate groups.

4. **The position of hydrogen is still left open to discussion.** It, being monovalent, can be placed either in Gr. I with the **alkali metals,** or in Gr. VII with the **halogens.**

Arguments **in favour of placing hydrogen in Gr. VII** *are* :—

(1) Like the halogens F and Cl, it is a *gas at the ord. temp.*

(2) Like the halogens, its molecules are *diatomic.*

(3) It may be replaced, atom for atom, from organic compounds by the halogens.

(4) Just as the metals form *halides* with the halogens, similarly some metals form *hydrides* with hydrogen.

(5) If it were placed in Gr. I, it would leave blank spaces in the table presupposing the existence of *six* still undiscovered elements lying between hydrogen and helium having atomic wts. between 1 and 4 which seems to be improbable.

(6) If it were placed in Gr. VII, no blank spaces would be left in the table.

Thus the position of the hydrogen is anomalous. Then again, hydrogen combines with *electro-negative* elements like the halogens to form acids in which it is *electro-positive* and is liberated at the cathode. It also combines with the *electro-positive* elements like sodium, calcium, lithium, etc. to give hydrides in which it is *electro-negative* and is liberated at the anode *e.g.*, when fused lithium or calcium hydride is electrolysed. In the third place, hydrogen combines with boron, silicon, etc. giving compounds which are *non-electrolytes* showing that hydrogen is here *non-polar*. Further, hydrogen exhibts all types of valency—*positive electro-valency, negative electro-volency* and *covalency*.

Hydrogen, therefore, belongs to no one group of the periodic table. Its proper position is at the head of the table, the *prototype* of the whole system.

Exercise

1. Write an essay on the periodic system. *C, U, 1925, '27, '42, '44, '46 ; Punj., 1900, '06 : Banaras,, '37 ; Nag, 1901.*

2, What are the defects of the periodic system ? Give examples.

3, Discuss the position of hydrogen and manganese in the periodic table. *Banaras, 1907.*

4. What do you understand by the word *'periodic'* in connection with the classification of elements ? *Punj , 1929 ; Bom, B. A.*

5. In the periodic table lead appears in the same vertical column with tin. Could you justify the arrangements by referring to the properties of their compounds ?

6, What are the main features of the periodic classification of the elements ? Indicate some of its important application, *C. U. 1941,*

CHAPTER XIII

HYDROGEN

Mol. formula, H_2. At. wt., 1. At. no., 1. Valency, 1.

History.—Cavendish (1756) was the first to prove that hydrogen was a distinct substance. It was then called *'Inflammable air'*, Lavoisier (1783) gave the name *Hydrogen* (*Water producer* : *Hydro=water*, *Genas=I produce)* to it.

Occurrence.—In the point of abundance, hydrogen occupies the eighth place among elements. In the free state, it occurs only in small quantities in volcanic gases, and in the upper region of the atmosphere. It is also present in the outer atmosphere of the sun. But it occurs mostly as compounds forming one-ninth by weight of weter and being almost universally present in all plant and animal tissues and in products obtained therefrom—fats, oils, sugars, starches, proteins, cellulose (wood and cotton), alcohol etc. It is also the constituent of all acids, alkalis, natural gas and petroleum.

Preparation

Hydrogen can be prepared from (1) acids, (2) water and (3) alkalis.

(1) **From acids.**—All metals which are more electropositive than hydrogen can set free the latter from dilute sulphuric acid, hydrochloric acid and many other acids.

The table below gives a list of metals arranged top to bottom in the decreasing order of their electropositivity which is measured by their tendency to lose electrons and pass into solution as positive ions. All the metals above hydrogen in the series can liberate hydrogen from dilute acids, such as dil. HCl and dil. H_2SO_4.

Table

(The activity series of metals.)

K Na Ba Ca Mg	Reacts with water ; reacts violently with acids
Al Zn Fe Cd	Reacts with steam ; reacts with acids readily.
Co Ni Sn Pb	Reacts slowly with acids. No action with water or steam.
H	
Cu Hg Ag Pt Au	No reaction with water, steam or acids.

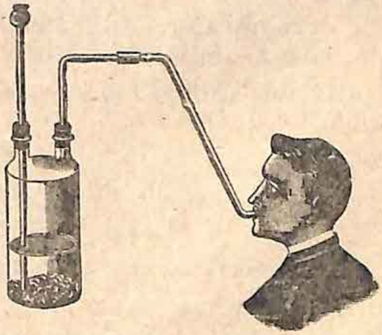
Laboratory preparation of hydrogen :

The action of zinc on dilute sulphuric acid is the basis of the laboratory method of preparation of hydrogen.

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$

Experiment :

Put a few pieces of granulated zinc in a two-necked Woulfe's bottle which is fitted up with a thistle funnel and a delivery tube. The apparatus is made airtight which can be tested by placing some water in the Woulfe's bottle and blowing through the delivery tube. Water rises in the thistle funnel. The end of the delivery tube is now closed with the tip of the tongue or by the finger. If the level of the water in the thistle funnel remains stationary, then



Fif, 32.—Testing whether the apparatus is airtight the apparatus is airtight. (fig. 32). Now put the end of the delivery tube under water in a pneumatic trough. (fig. 33).

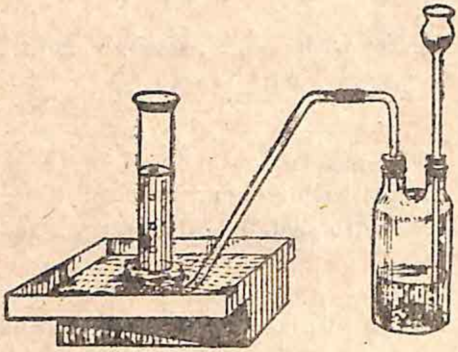


Fig. 33.—Preparation of Hydrogen

Dilute sulphuric acid is poured down the thistle funnel, the end of which should dip under the surface of the liquid. A brisk evolution of hydrogen takes place. The gas is allowed to escape for some time till all air from inside the apparatus is swept out. This precaution is necessary because hydrogen forms an explosive mixture with air. Now invert a gas jar completely filled with water over the trough and introduce the end of the delivery tube into it. Hydrogen collects in the gas jar by displacement of water. (fig. 33).

The hydrogen prepared as above contains many impurities such as H_2S, NH_3, PH_3, AsH_3, CO_2, SO_2, NO_2, moisture and nitrogen etc. The gas may be purified by passing it through a series of U-tubes containing the following substances in the order given below :—

1. Lead nitrate solution to absorb H_2S.
2. Silver sulphate solution to absorb PH_3 and AsH_3,
3. KOH to absorb SO_2, NO_2, CO_2 and
4. P_2O_5 to absorb moisture.

Nitrogen, however, cannot be so easily removed.

2. **From water.**—(i) Some metals decompose water to set free hydrogen gas (see activity series of metals).

(*a*) Metals which are strongly electrositive *e.g.*, sodium, potassium, calcium etc. decompose water at the ordinary temperature.

$$2Na + 2H_2O = 2NaOH + H_2$$
$$2K + 2H_2O = 2KOH + H_2$$
$$Ca + 2H_2O = Ca(OH)_2 + H_2$$

(*b*) Metals such as aluminium, iron etc., which are less electropositive decompose steam at a higher temperature and cannot react with water at the ordinary temperature. Red hot iron, for example, decomposes steam. $3Fe + 4H_2O = Fe_3O_4 + 4H_2$.

Ferrosoferric oxide.

Expt.—Boil water in a flask and pass the issuing steam through a porcelain tube filled with iron filings and heated to redness in a furnace. Connect the other end of the tube with a delivery tube. Introduce the end of the delivery tube in a *beehive* shelf on which is kept inverted a gas jar filled with water in a *pneumatic trough*

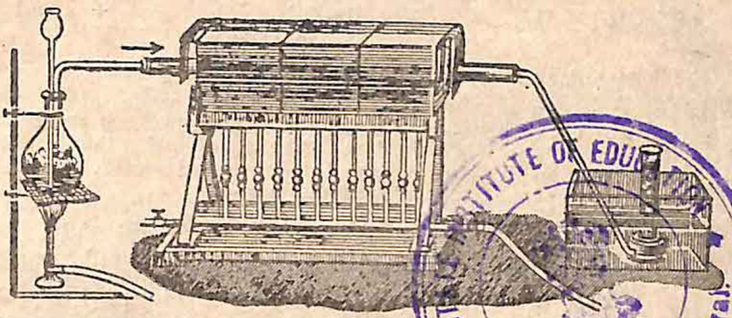


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Fig. 34—Preparation of Hydrogen by passing steam of ever red-hot iron.

(fig. 34). Steam is decomposed by red-hot iron and hydrogen is evolved which collects inside the gas jar.

(*c*) Metal such as copper, silver, mercury, lead etc., which are below or immediately above hydrogen in the activity series cannot decompose either water or steam under any condition.

(ii) **By electrolysis of water.**—Hydrogen is also obtained by the electrolysis of water which has been rendered conductor of electricity by the addition of a little acid or an alkali.

Expt. :

A glass basin containing two vertical pt. foils, fused at its bottom is half filled with water to which sulphuric acid (a few drops) is added. Two graduated tubes filled with acidulated water are inverted over the foils (fig. 35). The foils are now connected to the two ends of a battery and electric current is passed. Bubbles of gas collect in both the tubes by the displacement of water. It is found that the gas evolving at the cathode collects twice as fast as the gas which collects at the anode. On examination the gas at the cathode is found to be hydrogen and that at the anode oxygen.

$$2H_2O = \underset{\text{Cathode}}{2H_2} + \underset{\text{Anode.}}{O}$$

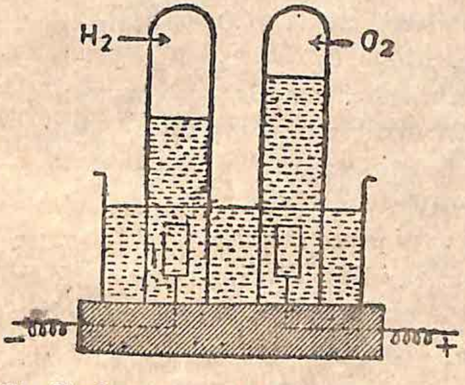


Fig. 35—Preparation of Hydrogen by Electrolysis of Water.

3. **From Alkalis.**—Hydrogen can also be prepared by boiling caustic soda or caustic potash solution with metals like zinc, aluminium, tin, etc. or with a non-metal like silicon.

$Zn + 2KOH = Zn(KO)_2 + H_2$
(Potassium zincate)

$2Al + 2NaOH + 2H_2O = 2NaAlO_2 + 3H_2$
(Sodium aluminate)

$Si + 2NaOH + H_2O = Na_2SiO_3 + 2H_2$
(Sodium silicate)

Manufacture or Technical Preparation of Hydrogen

Zinc is too expensive a substance to be used in the manufacture of hydrogen. Also, only 2 parts by wt. of hydrogen are obtained from 65 parts by wt. of Zinc. A *limited quantity* of hydrogen is obtained as a by product during the electrolysis of NaCl sol. In some circumstances, iron and steam method is used. But the *large amount* of commercial hydrogen is obtained from water-gas.

1. *From Steam and Iron* (*Lane Process*).—Steam is passed into retorts packed with iron and heated to red heat (600°—800°C) in a furnace. Steam is decomposed, Magnetic oxide of iron, Fe_3O_4 is formed and hydrogen is given off. The former is reduced by water-gas into iron which is used over again.

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2$$
$$Fe_3O_4 + 2(CO + H_2) = 3Fe + 2H_2O + 2CO_2.$$

2. *From Water-gas* (*Bosch Process*).—This method consists of *three* operations.

(i) Steam is passed into a layer of *red-hot* coke, when a mixture of carbon monoxide and hydrogen known as *Water-gas* is produced.

$$C + H_2O = CO + H_2.$$

(ii) Since it is very difficult to separate CO from H_2, water-gas is now mixed with steam, and the mixture is passed, under pressure, over a heated catalyst *viz.* ferric oxide, mixed with the *promoter* chromium oxide, the temperature being kept around 450°C. CO and steam react together giving CO_2 and Hydrogen. $CO + H_2O = CO_2 + H_2$.

(iii) The mixture of CO_2 and hydrogen, under high pressure, is next pumped into water. CO_2 is absorbed in water, while hydrogen passes on. Thus we get hydrogen from water-gas.

3. *From water by electrolysis*—Where cheap electricity is available very nearly pure hydrogen may be obtained by the electrolysis of water into which a little acid or more often a little alkali has been added to render it conductor of electricity. Hydrogen used in the production of Vanaspati (vegetable ghee) in India is usually obtained by this method.

Properties : Physical—It is a colourless, odourless and tasteless gas at the ordinary temperature and pressure. Hydrogen is difficult to liquefy (b. p. −252°C). Liquid Hydrogen can be frozen to a snow-like solid (m.p. −259°C) by evaporation under reduced pressure.

Hydrogen is only very slightly soluble in water, 100 c. c. of water dissolving 2 c.c. of hydrogen only at 0°C. It is much lighter than air ; in fact it is the lightest of all substances known. Balloons filled with hydrogen and also soap bubbles blown with it rise in the air automatically thus proving that hydrogen is lighter than air. Hydrogen can be poured upward. (fig. 36). (Density :—0·08987 gm. per litre at N. T. P.)

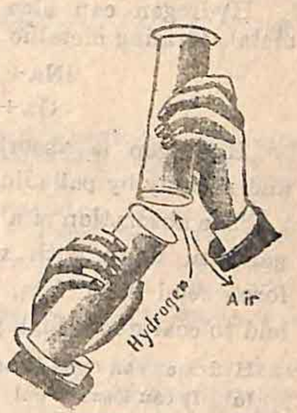


Fig. 36—Pouring Hydrogen upward

Chemical—Hydrogen is combustible, but not a supporter of combustion. A lighted chip when introduced into a jar of hydrogen is extinguished but hydrogen burns at the mouth (fig. 37) with a scarcely visible flame producing water.

Fig, 37—Hydrogen is combustible and not a supporter of combustison

Hydrogen forms an explosive mixture with oxygen. When two volumes of hydrogen and one volume of oxygen are mixed together and the mixture is ignited, the two gases combine immediately causing a violent explosion. The product is water, $2H_2 + O_2 = 2H_2O$. At ordinary temperatures, hydrogen does not practically react with oxygen unless kindled.

Expt.—Fill a soda-water bottle 2/3rd with hydrogen and 1/3rd with oxygen. Wrap the bottle up with a towel and apply a lighted taper to the mouth of the bottle. A violent explosion takes place immediately,

Combination between hydrogen and many other non-metals can also be brought about under suitable conditions.

$H_2 + Cl_2 = 2HCl$ *(in sun-light)*
Hydrogen chloride,

$N_2 + 3H_2 = 2NH_3$ *(under pressure and moderate temp.)*
Ammonia.

$2C + H_2 = C_2H_2$ *(when sparked)*
Acetylene.

Hydrogen can also remove these elements from their compounds. The process is called **reduction.**

Thus hydrogen reduces red-hot copper oxide to metallic copper.

$$CuO + H_2 = Cu + H_2O.$$

Hydrogen can also combine with some of the more electropositive metals forming metallic hydrides.

$$2Na + H_2 = 2NaH$$
$$Ca + H_2 = CaH_2.$$

Hydrogen is absorbed by metals like nickel, cobalt, iron, platinum and notably by palladium.

The absorption of a gas by a solid is known as **occlusion.** Hydrogen can unite with vegetable oils in presence of nickel catalyst to form semi solid fats, *Vanaspati* (an example is *Dalda*). It can also add to coal under high pressure to form artificial petroleum.

Hydrogen can react in any of the three ways noted below—

(*a*) It can lose its only electron to a more electro-negative element forming an electrovalent compound in which it exists as a positive ion.

$$H^{\cdot} = H + e$$

(*b*) It can gain an electron from a more electro-positive element forming an electrovalent compound in which it exists as a negative ion.

$$H^{\cdot} + e = H^-$$

(*c*) It can react by sharing of electrons forming covalent compounds.

$$H^{\cdot} + {}^{\cdot}X = H:X$$

With non-metals, hydrogen reacts according to (*a*) and (*c*) but mostly according to the latter forming covalent compounds which are gaseous at the ordinary temperature. The pair of electrons shared by the non-metal and hydrogen lies, however, closer to the non-metal on account of the greater electronegativity of the latter. $H \rightarrow : Cl$. In some cases, in solution, a severance of bond may take place giving rise to H^+ ions and the solution behaves as an acid. $H \rightarrow : Cl = H^+ + Cl^-$. With strongly positive metals, hydrogen reacts according to (*b*) $2Na + H_2 = 2Na + H^-$. The metallic hydrides are mostly electrovalent compounds like sodium chloride. On electrolysis hydrogen is set free at the anode.

Nascent State.—An element is said to be in the nescent (from Latin *nascor* to be born) *new-born* or *atomic* state when it is just liberated from a compound. As it is then in the *atomic state* and is liberated *under high pressure*, it is more reactive than ordinary molecular hydrogen.

Experiments to show that nascent hydrogen is a more powerful reducing agent than ordinary hydrogen.

(1) Make a sol. of potassium permanganate in water and acidulate it with *dil.* H_2SO_4. Pass hydrogen from a Kipp's apparatus into a portion of this solution. The pink colour of the solution is *not* discharged. Now add pieces of Zn and *dilute* H_2SO_4 *to the remaining portion* of the *same* solution. The pink colour gradually *disappears*.

$$2KMnO_4 + 3H_2SO_4 + 10H = K_2SO_4 + 2MnSO_4 + 8H_2O$$

Test of Hydrogen—(1) Hydrogen burns in air or in oxygen with a scarcely visible blue flame, with the formation of water *only*. (2) The product (*viz.* water) has no action on litmus sol or in lime-water (3) Hydrogen is *readily* absorbed by palladium.

Uses of Hydrogen.—Hydrogen is used as a reducing agent ; for the production of oxy-hydrogen flame, for *welding* and in limelight ; for filling balloons and air-ships ; for preparing ammonia and methanol synthetically and for *decolorizing*, *deodorizing* and *hardening* of fats and oils (*e.g.*, manufacture of vegetable products, etc.,) and for the production of synthetic petroleum from coal.

Exercise

1. Mention all the general methods of preparation of hydrogen. Give equation. Describe *one* method in detail giving a neat sketch of the apparatus for the preparation of hydrogen. *Mad*, *1936.*

2. Describe *three* experiments suitable for illustrating in a striking manner the extreme lightness of hydrogen. *Camb. Jun, : Pat., 1930.*

3. Under what conditions do oxygen and hydrogen combine to form water? How is hydrogen prepared from alkalis? *C. U., 1943 ; Punj., 1929.*

4. Why does hydrogen gas when poured out flow upwards? Why is it an excellent gas for filling balloons?

5. How is *pure* hydrogen prepared from ordinary zinc and H_2SO_4? What precautions should be taken in collecting and burning the gas? What is meant by occluded hydrogen? *C. U., 1935.*

6. Describe the laboratory method of preparation of hydrogen. State its important properties and uses. *Cal. Pre-U., 1962*

CHAPTER XIV

OXYGEN AND OZONE

Oxygen

Oxygen was discovered independently by Priestley and Scheele (1774) but they could not understand the real nature of the gas. Priestley obtained oxygen gas by heating red oxide of mercury. Lavoisier repeated this experiment of Priestley and showed that the gas formed the active part of air which took part in combustion. He named it oxygen as it was found to be the constituent of all acids known at that time (oxys = sour, genas = to produce).

Occurrence.—In the free state Oxygen occurs in the atmosphere, mechanically mixed with about four times its volume of nitrogen It is found in abundant quantities in combination with other elements in water, sand, etc. It is the most important constituent of earth's solid crust.

General Idea of Preparation.—Oxygen may be obtained (A) by decomposing **compounds rich in oxygen** : (B) by decomposing oxides of Hg, Ag, etc. ; (C) from **water** ; and (D) from **Air.**

(A) Laboratory Method of Preparation of Oxygen from Potassium chlorate and MnO_2.—*Expt.*—Take a mixture of powdered potassium chlorate and about $\frac{1}{5}$ its **weight** of manganese dioxide in a hard glass test tube fitted with a cork and a delivery tube. Introduce the end of the delivery tube into a gas jar filled with water and inverted over the *bee-hive shelf* of a pneumatic trough (fig. 38). Clamp the tube in a *slightly* inclined position and leave a passage over the mixture along the length of the hard glass tube for the escape of oxygen. **Now heat the tube carefully, when** $KClO_3$ is decomposed and oxygen is evolved.

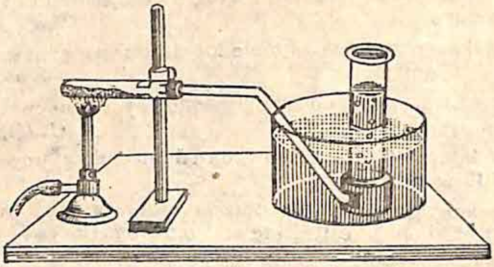


Fig. 38—Laboratory method of preparation of oxygen.

$$\begin{array}{ccc} 2KClO_3 & = & 2KCl + 3O_2 \\ [MnO_2] & & [MnO_2] \end{array}$$

Collection.—The evolved oxygen collects inside the gas jar by the displacement of water.

Precautions.—(1) Use comparatively pure MnO_2, otherwise particles of carbon present as impurity in MnO_2, will burn inside the tube and may cause explosion. (2) Leave a passage over the mixture. (3) Clamp the tube in a slightly inclined position so that the delivery tube is not choked. (4) Heat the tube uniformly.

N.B.—When large quantities of oxygen are required in the laboratory, instead of a hard glass test tube, a metallic tube or a metallic flask is used and the gas is collected in gas-holders.

The Role of MnO_2 in the Decomposition of $KClO_3$.

A small amount of MnO_2 when mixed with pot. chlorate brings about the decomposition of the latter at a temperature much lower than when pot. chlorate is heated alone.

Oxygen evolves freely at about 250°C below the m.p. of pot. chlorate. At the end of the reaction, the whole of MnO_2 can be recovered unchanged in mass and in chemical composition. MnO_2 acts as a catalyst. (see p. 40).

When heated alone, pot. chlorate first melts at 357°C and then evolves oxygen at 380°C, a portion changing into pot. perchlorate which requires still higher temperature for decomposition (610°C).

$$4KClO_3 = \underset{\text{Pot. Perchlorate}}{3KClO_4} + KCl.$$

$$KClO_4 = KCl + 2O_2$$

From other compounds rich in Oxygen.—Many other compounds rich in oxygen decompose to give off oxygen, when strongly heated :—

$2KNO_3$ (Potassium nitrate) $=$ $2KNO_2$ (Potassium nitrite) $+$ O_2

$3MnO_2$ (Manganese dioxide) $=$ Mn_3O_4 (Trimanganese tetroxide) $+$ O_2

$2Pb(NO_3)_2$ (Lead nitrate) $=$ $2PbO$ (Lead monoxide) $+$ $2N_2O_4+O_2$

$2KMnO_4$ (Potash permanganate) $=$ K_2MnO_4 (Potash manganate) $+$ MnO_2+O_2

1. From Lead nitrate.—*Expt.*—Heat lead nitrate strongly in a hard glass test tube which is connected with a U-tube kept immersed in a freezing mixtuture. Attach a delivery tube to the other limb of the U-tube, and introduce the free end of the delivery tube into a gas jar filled with water and kept inverted over water in pneumatic trough. Lead nitrate decomposes into lead monoxide, nitrogen dioxide and oxygen. The mixture of nitrogen dioxide and oxygen passes through the U-tube, where the former condenses, while oxygen collects in the gas jar.

2. From HNO_3 or H_2SO_4.—Concentrated sulphuric acid or concentrated nitric acid, when allowed to fall drop by drop on pumice stone, heated to redness in an earthenware, vitreosil or platinum vessel, decomposes thus—

$$4HNO_3 = 4NO_2 + 2H_2O + O_2.$$
$$2H_2SO_4 = 2SO_2 + 2H_2O + O_2.$$

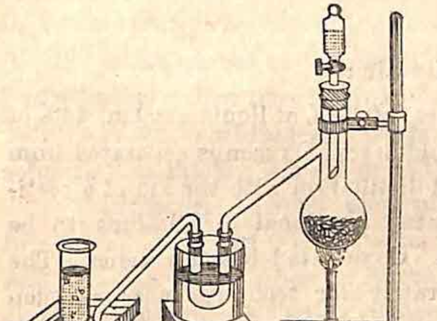


Fig. 39.—Oxygen from conc. H_2SO_4 or conc. HNO_3

Expt.—Take a distilling flask, half filled with pumic stone and fitted with a dropping funnel (fig. 39). Heat the flask, strongly and pour conc. H_2SO_4 *or* conc. HNO_3 drop by drop from the funnel. As each drop comes in contact with the *red-hot* pumice stone, the acid is decomposed. Allow the mixed gases to pass through a U-tube kept immersed in a freezing mixture, in which SO_2 *or* NO_2 is condensed, and oxygen passes on and collects in the gas jar over water.

3. From Sodium Peroxide Na_2O_2.—Take dry sodium peroxide in a conical flask fitted with a rubber cork and a dropping funnel containing water and a delivery tube (fig. 40). Allow water

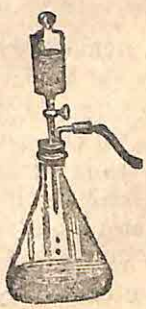


Fig. 40.—Oxygen from Na_2O_2

to fall on the peroxide drop by drop. A rapid stream of oxygen is evolved *without the application of heat.* $2Na_2O_2 + 2H_2O = 4NaOH + O_2$.

(B) When mercuric oxide or silver oxide is heated, we get oxygen

$$2HgO = 2Hg + O_2 \parallel 2Ag_2O = 4Ag + O_2$$

(C) *By electrolysis of water*.—Electrolyse water acidulated with *dil.* HCl or *dil.* H_2SO_4 *(at the ordinary temp.)* in a water Voltameter. Water is decomposed. Hydrogen is liberated at the cathode while oxygen is liberated at the anode and collects inside the tube containing the anode. Remove the tube and hold a *glowing* chip of wood in the mouth of the tube. The glowing chip is *rekindled.*

Manufacture of Oxygen

Industrial sources of Oxygen are mainly two : (1) Liquid air and (2) to a small extent electrolysis of water.

Formerly a technical process known as **Brin's process** was used, but it is now obsolete.

Manufacture of Oxygen from liquid air :

Liquid air is, chiefly a mixture of 54% of liquid oxygen, 44% of liquid nitrogen with about 2% of liquid argon. Oxygen is separated from nitrogen by a process of fractional distillation with the aid of a rectifying column which enables repeated fractional distillations to be carried out in a single operation. Oxygen is left as a residue. The nitrogen given off is collected separately for technical use. Oxygen obtained by this process is very nearly pure containing mainly a small quantity of argon as an impurity.

The oxygen gas is compressed by pumps into steel cylinders.

Boiling-point of liquid Oxygen = −182·9°C.
Boiling-poinf of liquid nitrogen = −195·7°C.

Properties

Physical.—Oxygen is a *colourless*, *tasteless*, *odourless* gas. It is the only gas that can support respiration and is essential to the life of animals. It is slightly *soluble in water*, which dissolves 4% by vol. of oxygen at 0°C ; hence fish and other aquatic animals can live in water. Oxygen thus serves a very important function in the economy of nature. Metals like gold, silver, platinum and palladium can *absorb* oxygen at a high temp. Molten silver absorbs oxygen which it again gives up on cooling.

Chemical.—Oxygen unlike hydrogen is not inflammable but is a supporter of combustion. It is very active. It combines with almost all elements (except helium, argon etc.).

Experiments to illustrate the important properties of Oxygen —

(*a*) Introduce a *glowing* chip of wood into a jar of oxygen. The chip is *rekindled i.e., bursts into flame.*

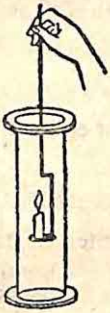


Fig. 41—Deflagrating spoon.

(*b*) Place a lighted candle on a *deflagrating spoon* (fig. 41) and then introduce it into a jar of oxygen. The candle continues to burn in the gas *more brilliantly* than it does in air. Now pour *clear* lime-water into the jar and shake well. Lime-water turns milky. This shows that CO_2 is produced when a candle burns in oxygen.

(*c*) Repeat the last expt, with a piece of *glowing* charcoal instead of a lighted candle. Charcoal burns *brightly* producing CO_2.

(*d*) Heat a piece of sulphur on a deflagrating spoon when sulphur burns feebly. Now insert it into a jar of oxygen. Sulphur burns with a brilliant bluish white light producing SO_2. Pour a little *blue* litmus solution into the jar, the colour of the solution turns *red.*

(*e*) Introduce burning phosphorus taken on a deflagrating spoon into a jar of oxygen ; Phosphorus burns with a dazzling white light. Add *blue* litmus sol. when it turns *red.* Phosphorus burns in oxygen giving phosphorus pentoxide which reacts with water producing phosphoric acid. This acid turns *blue* limus *red.*

$$4P + 5O_2 = 2P_2O_5$$
$$2P_2O_5 + 6H_2O = 4H_3PO_4$$

(*f*) Heat a piece of sodium on a deflagrating spoon and introduce the burning metal into a jar of oxygen ; the burning metal burns more brilliantly in the gas. Now pour *red* litmus solution into the jar. The colour of litmus turns *blue.*

$$8Na + 3O_2 = 2Na_2O + 2Na_2O_2$$
$$2Na_2O + 2H_2O = 4NaOH$$
$$2Na_2O_2 + 2H_2O = 4NaOH + O_2$$

(*g*) Tip a bundle of iron wire with burning sulphur and then plunge it into a jar of oxygen. Iron wire burns with brilliant *scintillation* producing magnetic oxide of iron.

$$3Fe + 2O_2 = Fe_3O_4$$

(*h*) Fill a gas-measuring tube with oxygen and invert it over alkaline potassium pyrogallate solution. The gas is absorbed and the solution slowly rises up the tube.

(*i*) Repeat the same experiment with freshly prepared ammoniacal cuprous chloride solution. The solution absorbs oxygen and it rises up the tube, and becomes deep-blue in colour.

Oxides

An Oxide is a binary compound of Oxygen and another element.

Classification of Oxides

(i) **Acidic** oxides,	(ii) **Neutral**	(iii) **Basic** oxides	(iv) **Amphoteric**	(v) **Peroxides**
also called Anhydrides They are generally oxides of non-metals. **They form acids** with water and neutralize bases *e.g.*, $P_2O_5+3H_2O$ phosphorous anhydride $=2H_3PO_4$ Phosphoric acid SO_3+H_2O Sulphuric anhydride $=H_2SO_4$ Sulphuric acid	oxides. They do not give acids with water and do not act as bases *e.g.*, NO. H_2O.	are generally oxides of metals. They neutralise acids to give salts and water *e.g.* $CuO+H_2SO_4$ $=CuSO_4+H_2O$ $CaO+2HCl$ $=CaCl_2+H_2O$ Some of them, with water give hydroxides of metals which in solution in water, turn *red* litmus *blue* *e.g.*, Na_2O+H_2O $=2NaOH$ K_2O+H_2O $=2KOH$. $CaO+H_2O$ $=Ca(OH)_2$	oxides. They behave both like acidic and basic oxides *e.g.*, ZnO. SnO_2, Al_2O_2, etc. ZnO dissolves in acids to produce Zinc salt. Therefore, it is *basic* in character. ZnO dissolves in *fused* alkalis to give Zincates. Therefore, it is *acidic* in character.	Formerly they included all those oxides which contained more Oxygen than either the acidic or the basic oxides. At present by the term peroxide we mean only *true peroxides* which, with dilute acids, give H_2O_2 in cold *e. g.* Na_2O_2, BaO_2, etc.

Tests—

(1) Oxygen rekindles a glowing chip of wood (*Cf.* N_2O).

(2) It produces brown fumes with nitric oxide (*Cf.* N_2O).

(3) It is absorbed by alkaline pyrogallate sol. (giving a *brown* solution), and ammoniacal cuprous chloride sol. (giving a *deep-blue* solution).

Use.—Oxygen is used for artificial respiration ; for the generation of oxy-hydrogen and oxy-acetylene flames ; and in aviation.

Absorbents :—(i) Alkaline pyrogallate and (ii) ammoniacal cuprous chloride solution.

The Oxy-hydrogen Flame.—The oxy-hydrogen flame is generated by burning hydrogen gas at the mouth of a specially constructed blow-pipe called the oxy-hydrogen blow-pipe and feeding the flame with oxygen.

The Oxy-hydrogen Blow-pipe.—The blow-pipe consists of two metal tubes connected together by means of a Y-tube (fig. 42) and soldered perfect air-tight. The tubes are connected with cylinders containing hydrogen and oxygen respectively. The stop-cock of the tube carrying hydrogen is first opened. The gas is allowed to escape for some time and is then lighted at the mouth of the blow-pipe. Now the stop-cock of the tube supplying oxygen is gradually opened. The maximum temperature 2800°C is obtained when the volumes of hydrogen and oxygen are taken in the proportion of *two to one.*

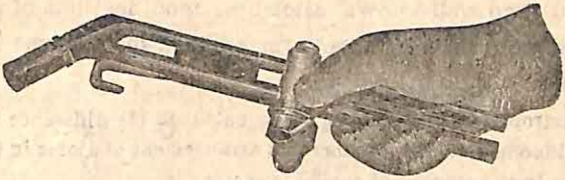


Fig. 42—Oxy-hydrogen blow-pipe.

Oxy-acetylene Flame.—Instead of hydrogen, it is the flame of burning acetylene, fed with oxygen. The temp. is *higher* than that of the oxy-hydrogen flame (3200°C).

Allotropy

When oxygen (or air) is subjected to silent electric discharge, a characteristic fishy odour is perceived, with which every one who has had to do with electrostatic machines or induction coil is familiar. The odour is due to the production of a gaseous substance known as *ozone.* Since ozone can be produced from pure dry oxygen by sparking alone, it proves that ozone is only a special form of oxygen. Ozone, however, differs from ordinary oxygen in many of its physical and chemical properties. Ozone is said to be an **Allotropic Modification of Oxygen.**

Definition of Allotropy : The property by virtue of which one element may exist in two or more different forms which differ more or less in physical as well as chemical properties is known as Allotropy.

The less common forms are called the allotropic modifications of the commoner form.

Many elements, besides oxygen occur in allotropic forms. Diamond, graphite, charcoal (wood and animal), lamp black, coke and gas carbon are different forms of the same element, Carbon.

Sulphur also occurs in allotropic forms, such as rhombic sulphur, prismatic (or monoclinic) sulphur, plastic sulphur, and milk of sulphur. There are also two well-known allotropic modifications of phosphorus namely, yellow (or white) phosphorus and red phosphorus (see respective elements).

Causes of Allotropy :—It is variously attributed to (1) difference in crystalline structures, (2) difference in the number and arrangement of atoms in the molecules and (3) difference in the amount of available energy.

Ozone, O_3

Ozone is a form of oxygen. A molecule of ozone contains three atoms of oxygen *i.e.*, its molecular formula is O_3 whereas a molecule of oxygen has only two atoms of oxygen *i.e.*, O_2. Ozone, however, differs in many ways physically and chemically from ordinary oxygen.

Ozone as has been discussed above is an allotropic modification of oxyen.

Occurrence.—Ozone occurs in small quantities in sea-air. It is formed when an electric machine is at work ; during thunder-storm and at the time of the electrolysis of acidulated water.

Ozone is prepared when dry oxygen (or air) is subjected to silent electric discharge, in a special apparatus (Siemen's Ozoniser). $3O_2 = 2O_3$.

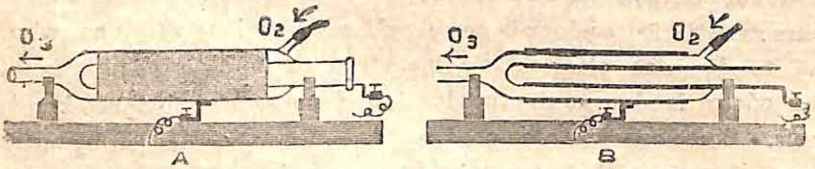


Fig. 43—Siemens' Ozone Apparatus. (A—General view. B.—Sectional view)

Properties

Physical.—Ozone is a *pale-blue* gas having a *bad fishy smell.* Liquid ozone is *deep-blue* in colour, It is *more* soluble in water than oxygen. It readily dissolves in oil of turpentine.

Chemical.—Ozone is more active than oxygen. It is a powerful oxidising agent (see below). It oxidises black lead sulphide into white lead sulphate.

$$\begin{aligned} PbS + 4O &= PbSO_4 \\ 4O_3 &= 4O_2 + 4O \\ \hline PbS + 4O_3 &= PbSO_4 + 4O_2 \end{aligned}$$

Ozone sets free halogens (except fluorine) from halogen acids.

$$\begin{array}{rcl} 2HX+O & = & H_2O+X_2 \\ O_3 & = & O_2+O \\ \hline 2HX+O_3 & = & H_2O+X_2+O_2 \quad (X=\text{a halogen}) \end{array}$$

It liberates iodine from potassium iodide solution.

$$\begin{array}{rcl} 2KI+O & = & K_2O+I_2 \\ O_3 & = & O_2+O \\ K_2O+H_2O & = & 2KOH \\ \hline 2KI+H_2O+O_3 & = & 2KOH+I_2+O_2 \end{array}$$

It bleaches vegetable colour by oxidation.

Ozone is decomposed completely into oxygen when heated to 250° to 300°C.

$$2O_3=3O_2$$

Test.—(i) Ozone has a fishy odour. (ii) it turns starch iodide paper blue, and (iii) it is absorbed by turpentine oil.

Use.—Ozone is used for—(i) purifying and sterilizing water ; (ii) purifying air (especially in under-ground railways) ; (iii) bleaching oils, waxes, etc., ; and (iv) for oxidizing organic compounds.

Oxidation and Reduction

Oxidation.—In a limited sense, oxidation means *the process of direct union with oxygen.* When hydrogen, magnesium, phosphorus, carbon, iron, sulphur, etc. burn in oxygen to form their oxides, we say that they have all undergone *oxidation.*

Oxidation may also mean *taking away of hydrogen.* When chlorine is prepared by heating manganese dioxide with conc. HCl, we say that MnO_2 has *oxidized* HCl. Here oxygen of MnO_2 has *taken away hydrogen* from HCl Thus oxidation, *in the above cases*, consists in either *adding* oxygen or *removing* hydrogen.

Now, oxygen belongs to a class of elements which we call non-metallic or *electro-negative* elements. We should not, therefore, restrict the term **oxidation** to actions involving oxygen alone, but should make it broad enough to include actions involving other *like* electro-negative elements (*viz.* chlorine, bromine, iodine, etc.). Thus, when ferrous chloride is *oxidized* into ferric chloride, stannous chloride is *oxidized* into stannic chloride, mercurous chloride into mercuric chloride, ferrous sulphate into ferric sulphate, etc., we increase the amount of the non-metallic (*electro negative*) part in the molecule as *also the valency of the metal.*

$$\begin{array}{rcl} 2FeCl_2+Cl_2 & = & 2FeCl_3 \\ SnCl_2+Cl_2 & = & SnCl_4 \end{array}$$

$$6FeSO_4+3H_2SO_4+3HNO_3=3Fe_2(SO_4)_3+4H_2O+2NO$$

Considered from all these points of view, oxidation means—

(i) *Addition of Oxygen.*

(ii) *Removal of Hydrogen.*

(iii) *Increasing the proportion of the electro-negative (i.e., non-metallic) element or decreasing the proportion of the electro-posiive (i.e., metallic) element in the substance.* That is to say.

Oxidation is the process which introduces or increases the proportion of the electro-negative atoms or groups in an element or a compound, or removes or diminishes the proportion of a an electro-positive atoms or groups in a compound.

Reduction.—It ordinarily means removal of oxygen. Thus when copper oxipe is heated in a current of hydrogen, it is *reduced* into metallic copper *i. e.*, oxygen is removed from CuO.

Reduction also means *addition of hydrogen.* When H_2S is passed into chlorine-water, chlorine is reduced to HCl *i.e.*, hydrogen is added to chlorine.

But when $FeCl_3$ is reduced to $FeCl_2$ by *nascent* hydrogen, what takes place is that the proportion of the electro-negative or non-metallic chlorine, present in ferric chloride, is *decreased.* Also trivalent ferric iron is changed into divalent ferrous iron.

Considered from all these points of view, reduction, means—

(i) *Addition of hydrogen.*

(ii) *Removal of oxygen.*

(iii) *Decreasing the proportion of the electro-negative (i.e. non-metallic) element or increasing the proportion of the electro-positive (i e. metallic) element in a substance.* That is to say,

Reduction is the process which introduces or increases the proportion of the electro-positive atoms or groups in an element or a compound or removes or diminishes the proportion of the electro-negative elements or groups in a compound.

Oxidation and reduction in the light of electronic theory. According to the electronic theory, when a substance loses electrons, it is oxidised, and when it gains electrons, it is reduced.

The **oxidation** is, therefore, a process whereby an atom or an ion loses electrons and the reverse process whereby an atom or ion gains electrons is **reduction.**

Whenever something is oxidised, something else must be reduced.

Oxidising agents are acceptors of electrons while **reducing agents** are donors of electrons. Total number of electrons lost by the oxidising agent must be the same as the total number of electrons gained by the reducing agent.

The reactions involving oxidation and reduction (the two must occur together) is known as *reduction-oxidation* (or *redox*) reactions. Some of the most important chemical reactions belong to this type.

Illustrations.—

(*a*) When sodium metal reacts with chlorine to form sodium chloride, chlorine gains an electron lost by sodium. Chlorine by gaining an electron is reduced and sodium by losing an electron is oxidised.

$$\begin{array}{rcl} \mathrm{Na} & = & \mathrm{Na^+} + e \\ \mathrm{Cl} + e & = & \mathrm{Cl^-} \\ \hline \mathrm{Na} + \mathrm{Cl} & = & \mathrm{Na^+Cl^-} \\ \text{Or,}\quad \mathrm{2Na} + \mathrm{Cl_2} & = & \mathrm{2Na^+Cl^-} \end{array}$$

(*b*) When stannous chloride solution is mixed with ferric chloride solution, a transference of electrons takes place from the stannous ions to the ferric ions. Each stannous ion loses two electrons to two ferric ions, each receiving one electron. Stannous ions by losing electrons are oxidised to the stannic state and ferric ions by accepting them are reduced to the ferrous state.

$$\begin{array}{rcl} \mathrm{Sn^{2+}(ous)} & = & \mathrm{Sn^{4+}(ic)} + 2\mathrm{e} \\ \mathrm{2Fe^{2+}(ic)} + 2\mathrm{e} & = & \mathrm{2Fe^{2+}(ous)} \\ \hline \mathrm{Sn^{2+}(ous)} + \mathrm{2Fe^{2+}(ic)} & = & \mathrm{Sn^{4}(ic)} + \mathrm{2Fe^{2+}(ous)} \end{array}$$

(*c*) In electrolysis, ions are discharged at cathode by gaining electrons. Hence they are reduced. We, therefore, speak of cathodic reduction, At anode, ions are discharged by giving up electrons. Hence, they are oxidised. We therefore, speak of anodic oxidation.

Exercise.

1. What expianation has been advanced of the action of manganese dioxide in the preparation of oxygen from potassium chlorate ? What is catalysis ? What is a positive catalyst ? *Cam. Jun., Pat., 1919 ; C. U., 1932, '41, '46.*

2. What are oxides ? How would you classify them ? Describe the preparation and properties of one member of each class. How will you classify NO_2, BaO_2, MnO_2, ZnO, Pb_3O_4 ? *Cam. Jun., Mad., 1925 ; Punj., 1926.*

3. How wouid you show that oxygen can be obtained from lead nitrate ? Sketch the apparatus. Give equation. *C. U., 1934, '41*

4. Describe how you would oxidize ferrous sulphate to ferric sulphate and how you would show that the oxidation was complete.

5. Is it necessary that an oxidizing agent shouid contain oxygen ? Give your reasons. *Cam. Jun.*

6. How will you determine whether a substance is an oxidizing or a reducing agent ? 'Oxidation never takes place without reduction'. Explain.

7. What takes place when the products of combustion of carbon, sulphur, and phosphorus are respectively brought into contact with water ?

8. What experiments tend to show that ozone is more active oxidizing agent than oxygen ? *Calcutta Presidency College, 1943 ; Bom., 1918.*

9. How is ozone prepared ? What are its uses ?

10. How will you obtain a sample of oxygen from sodium peroxide ? Sketch the apparatus. *Pat., 1911 ; '26, '38.*

11. Describe how oxygen is manufactured from liquid air ? *C. U., 1938.*

12. Explain and Illustrate.
—Oxidation and Reduction. *Cal. Pre-U. 1961 ; '62, '67.*

13. Write Short notes on Allotropy. *Cal. Pre-U., 1961, '66.*

14. Explain the phenomena of Oxidation and Reduction with suitable examples. Illustrate the oxidising action of Cl_2 and SO_2 and reducing action of H_2S. *Cal. Pre U. 1970*

CHAPTER XV

WATER AND HYDROGEN PEROXIDE

Water (*Hydrogen monoxide*)

Formula, H_2O. Mol. wt., 18. Vapour density, 9. Sp. gr., 1.

History.—Until the time of Cavendish water was considered to be an element. In 1781 he showed that water was produced by exploding a mixture of inflammable air (*hydrogen*) and oxygen. Lavoisier in 1783 repeated Cavendish's expt. and also proved the presence of oxygen in water by passing steam through a red-hot gun barrel, when inflammable air and magnetic oxide of iron were produced. Thus water was proved to be a compound.

Occurrence.—It is widely distributed in nature. It occurs

(1) as **Solid.**—In the form of ice, snow, and as water of crystallization in some naturally occuring compounds.

(2) as **Liquid.**—In the form of water : $\frac{3}{4}$ths of the surface materials on the crust of the earth consist of water.

(3) as **Water-vapour.**—It is present in the atmosphere.

Natural water.—Chemically pure water is unknown in nature. Natural waters are liable to contain various kinds of impurities depending upon the sources from which they are obtained.

Classification of Natural Waters

Natural waters are classified in different ways depending upon—

(A) The sources from which they are obtained, *viz.*, Rain-water, River-water, etc.

(B) Fresh water and Mineral water.

(C) The **behaviour towards soap,** *viz.*, Hard water & Soft water.

(D) Whether it is potable or non-potable.

(A) Classification of Natural waters according to the sources from which they are obtained, and in order of their purity—

They are :—(1) **Rain-water,** **Spring and Well water,** (3) **River and Brook-water** and (4) **Sea-water.**

(1) **Rain-water** —It being naturally distilled water, is the purest form of natural water. Still it contains various kinds of impurities *e.g.*, oxygen, carbon dioxide, traces of ammonia, nitric and nitrous acids, dust particles containing salts and organic matter, which it derives while falling through the atmosphere. Near manufacturing towns H_2SO_4 and SO_2 may also be present. The first shower may remove a greater portion of these impurities with the result that the subsequent showers are comparatively pure.

(2) **Spring and Well-water.**—They differ from river-water (*see below*) in having undergone filtration through porous *strata*, and consequently, do not contain suspended impurities. The water is clear and transparent when it percolates out of the soil. It, however, contains many impurities such as salts of Ca, Mg, Na, K, sometimes Fe, and other substances which it dissolves from the soil.

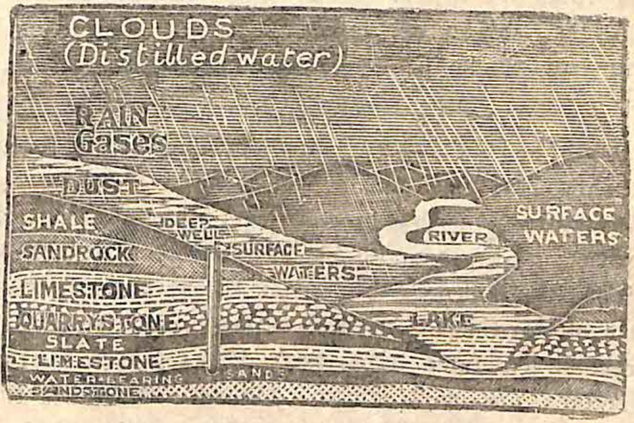


Fig. 44.—Sources of Natural waters.

Spring water and well-water may also contain H_2S, CO_2 and other gases. Hot Spring at Sitakunda, Rajgir and other places in India contain water having a temperature much higher than the ordinary temp. and sometimes appear boiling due to the escape of hot gases from crevices inside the spring.

(3) **River and Brook-water.**—River and brooks are generally fed by rain-water which derive impurities both soluble and suspended,

organic and inorganic, while passing over the soil. Hence it is *generally* turbid.

(4) **Sea-water.**—It contains the largest amount of dissolved impurities like chlorides, sulphates, carbonates, bromides and iodides of sodium, potassium, calcium, and magnesium, of which common salt is the most important. Sea-water contains about 3·6% of total solids of which 2·6% is common salt.

(B) Classification of Natural water based upon the amount of dissolved impurities.—Thus classified Natural waters are—

(i) *Mineral water*, and (ii) *Fresh water*.

(i) Mineral Water.—When spring water happens to contain excessive quantities of solid and gaseous substances in solution which impart to it a peculiar taste or a specific property, the spring water is then termed a mineral water.

Mineral water may be—(i) *saline*—due to the presence of NaCl; (ii) *alkaline*—due to the presence of $NaHCO_3$; (iii) *bitter*—due to the presence of $MgSO_4$; (iv) *aerated*—due to the presence of CO_2; (v) *sulphuretted* (hepatics *i.e.*, *useful to liver*) —due to the presence of H_2S; (iv) *chalybeate* [*i.e.*, *containing iron*—due to the presence of $Fe(HCO_3)_2$]; (vii) *Silicious*—due to the presence of silica and alkaline silicates and (viii) *Hot*—due to the presence of dissolved hot gases.

(ii) Fresh-water.—It is natural water which does not contain much impurities in solution.

(C) Classification of Natural waters according to their behaviour towards soap.—(i) Soft water, and (ii) Hard water.

Soft water and Hard water

Soft water.—It is that kind of water which easily forms a lather with ordinary soap.

Hard water.—It is that kind of water which does not easily give a lather with ordinary soap (due to the presence of soluble calcium and magnesium salts), but does so after much soap is consumed.

Cause of Hardness.—Natural waters contain salts of metals as the non-volatile soluble impurities. *When they are salts of calcium and magnesium, the sample of water is* **hard**. Therefore, **the cause of hardness is the presence of the soluble calcium and magnesium salts, like calcium and magnesium bicarbonates, sulphates, and chlorides in water.**

Two different kinds of hardnsss ; Temporary and Permanent.

Temporary hardness of water is due to the presence of *bicarbonates* of Ca or Mg or both in solution. The hardness is called **temporary, for it can be removed by easy means like boilling etc.**

Permanent hardness of water is due to the presence of *sulphates* and *chlorides* of Ca and Mg. The hardness is called permanent, for it cannot be removed by easy means like boiling, etc.

Removal of Hardness—Softening of Hard water

It is clear that the hardness of water is due to the presence of *soluble* Ca and Mg salts. If these *soluble salts* are, *somehow or other*, converted into *insoluble* substances which can be easily removed then the water left will be soft. This is the *principle* upon which the softening of *hard* water depends.

Removal of Temporary Hardness

1. *By boiling*—Temporarily hard water is *saftened* by boiling, so that the *soluble* Ca and Mg *bi-carbonates* present are converted into the *insoluble carbonates* of Ca and Mg.

$$\underset{\text{(sol.)}}{Ca(HCO_3)_2} = \underset{\text{(insol.)}}{CaCO_3} + H_2O + CO_2$$

$$\underset{\text{(sol.)}}{Mg(HCO_3)_2} = \underset{\text{(insol.)}}{MgCO_3} + H_2O + CO_2$$

2. *By Clark's process.*—By this process, temporarily hard water is *softened* by the addition of the *requisite amount* of lime in the form of lime-water or milk-of-lime. $Ca(HCO_3)_2$ is precipitated as $CaCO_3$; while, if $Mg(HCO_3)_2$ be present, double the amount of lime is added, when sparingly soluble $Mg(OH)_2$ is formed.

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O$$

$$Mg(HCO_3)_2 + 2Ca(OH)_2 = 2CaCO_3 + Mg(OH)_2 + 2H_2O$$

Removal of Permanent Hardness

This kind of hardness cannot be removed either by boiling or by Clark's process. Permanent hard water is *softened* by converting the *soluble* sulphates and chlorides of Ca and Mg present into *insoluble* carbonates of Ca and Mg by the addition of sodium carbonate (*washing soda*) to it.

$$CaCl_2 + Na_2CO_3 = CaCO_3 + 2NaCl$$

$$MgSO_4 + Na_2CO_3 = MgCO_3 + Na_2SO_4.$$

Permutit Process of Removal of Hardness—Temporary and Permanent, at the same time.—In Gan's Permutit process, bodies, called permutits, which are artificially prepared mixture of hydrated Al-silicate, Na-silicate, etc., (or the naturally occuring minerals, *Zeolites*) are employed. The name permutit (from Lat.

Permutare = *exchange*) has been given to the mixture for it can easily exchange bases (fig. 45).

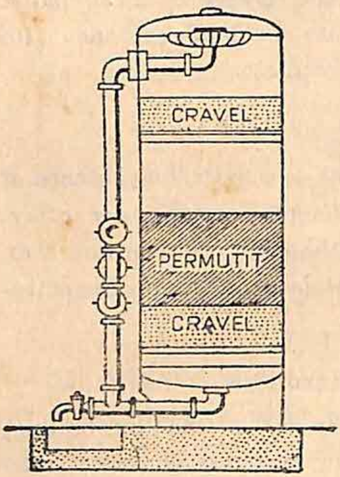


Fig. 45—Permutit filter

Principle.—The method depends upon the fact that when hard water is filtered through permutit, the sodium salt, present in it, reacts with soluble Ca and Mg salts, present in hard water, producing insoluble Ca and Mg compounds, and the filtrate, being *altogether* free from Ca and Mg salts, is soft and has no soap-destroying property.

*Sodium permutit + Ca-salt.
= Ca-permutit + Na-salt.
Sodium permutit + Mg-salt.
= Mg-permutit + Na-salt.

When the permutit, due to long use, is exhausted, it is *reactivated* by treatment with a solution of common salt. Thus permutit can be used over and over again.

$$\text{Ca-permutit} + 2NaCl = 2\text{Na-permutit} + CaCl_2.$$
$$\text{Mg-permutit} + 2NaCl = 2\text{Na-permutit} + MgCl_2.$$

Hard water versus soft water.—*Soft water has the following advantages over Hard water* :—(i) No fur is produced in boilers at the time of raising steam : production of fur causes a great waste of fuel ; (ii) boilers are not damaged when soft water is used ; and (ii) for washing purposes, *much less* soap is required when soft water is used than when hard water is used.

Hard water has the following advantages over soft water :—(i) For drinking purposes, very soft water should not be used, for some quantities of calcium salts are required for the growth of the human body, especially in the case of children ; (ii) Soft water dissolves lead much more readily than hard water. Therefore, there is *less* chance of *lead poisoning* with hard water than with soft water.

(D) Natural waters may also be classified into *potable water* and *non-potable water*.

Uses of Natural waters—

(1) For drinking purposes;
(2) As a feed-water for boilers ;
(3) For washing, and other household purposes ;
(4) In photography ; in the preparation of medicines ; and in Chemical Works, Factories, Chemical Analysis ;
(5) In irrigation ; and (6) As a solvent.

---

* Permutit, hydrated sodium-silico-aluminate is written as sodium permutit for convenience.

Drinking water (*potable water*)—For drinking purposes, water should be *clear*, *colourless* (*i.e.*, free from suspended impurities), *free from organic* impurities, especially germs of diseases arising from sewage contamination or decaying animal or vegetable matter, and should be of a *pleasant taste*. That is to say, it must be free from pathogenic bacteria. It need not however, be absolutely pure and may have *small quantities* (and not excess) of salts dissolved in it. Distilled water and rain-water are *flat* and *insipid* and are unsuitable for drinking purposes ; but spring water, having a characteristic *freshness*, is found to be most suitable.

Purifying Natural Waters for drinking purposes.—When however, natural waters, obtained from other sources, have to be used for drinking purposes, they must be purified before use. The insoluble or suspended impurities present in such samples of water are removed by **settling** and **filtration**, and the *filtered water* is *sterilized*.

(A) **On a small scale,** filtration of water for drinking purposes may be effected by the following **domestic** or other forms of **filters**—

The Old Pitcher-filter Method—This consists of four earthenware pitchers (*Kalsi*), the first three having each a hole at the bottom, and placed one upon the other on a wooden framework, still seen in remote Railway Stations in India. The topmost *pitcher* contains the unfiltered water to which sometimes alum is added. The water from this pitcher drops into the *2nd pitcher*, half-filled with powdered **charcoal**. From the *2nd pitcher* water drops into the *3rd pitcher* containing **gravel** and **fine sand**. The lowermost **pitcher** acts as a reservoir for the *filtered water*.

(B) **When large quantities of water** are required to be purified for drinking purposes as in a town supply, the process of settling mud and other suspended impurities is hastened by the addition of alum to water in a series of settling tanks. The water is then filtered through layers of fine sand, coarse sand and gravels in filter beds (Fig. 46). Finally sterilisation of the filtered water is effected by killing disease producing germs by agents such as (a) pot. permanganate, (b) chlorine in the form of bleaching powder, (c) ozone, (d) ultra violet light or (e) by aeration, that is by forcing the water in the form of a spray so that it may come in contact freely with oxygen of air and be exposed to the ultra violet light of the sun. The sterilised water is then pumped to an overhead tank from where it is supplied to the consumers.

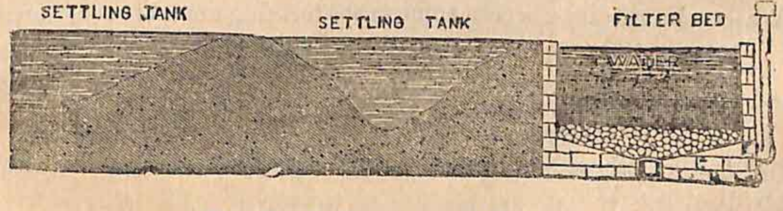


Fig. 46—Settling tank and filter bed

Properties of water : Physical.—Water, in the pure state, is a clear, transparent, and tasteless liquid at the ordinary temperature. It is colourless in thin layers but appears bluish-green when viewed in bulk. It gives off vapour at all temperatures and leaves no residue on evaporation. Its specific gravity is 1. *Effect of heat.*—Water is a bad conductor of heat. Under 760 mm. pressure, water boils at 100°C. When cooled, water gradually contracts until it reaches the temp. of 4°C. At this temperature water has maximum density, for here it *expands* both when *cooled* and *heated*. When the temperature is further lowered, it solidifies into ice at 0°C. It is also a bad conductor of electricity. Water is a very good solvent and dissolves many substances both at low and at high temperatures. Conc. H_2SO_4, solid KOH, NaOH etc. dissolve in water with *evolution of heat* ; while NH_4Cl, NH_4CNS, etc., disslove in water with *absorption of heat*. Water is a remarkable *ionizing solvent*. *Electrolytes* dissolve in it and dissociate into ions.

Chemical.—Water is neither acidic nor basic to litmus. It is, therefore, a neutral liquid.

Action of metals on water—Metals like K, Na, Ca decompose water at the ordinary temperature. Magnesium and iron when strongly heated, can decompose steam ; while metals like silver, mercury, tin, etc. have got no action on water, either at the ordinary temperature or at higher temperatures.

Action of water on oxides :—

Water acts upon anhydrides with the formation of oxy-acids

$SO_3 + H_2O = H_2SO_4$ (sulphuric acid)

$P_2O_5 + H_2O = 2HPO_3$ (meta-phosphoric acid)

$P_2O_5 + 3H_2O = 2H_3PO_4$ (ortho-phosphoric acid)

and combines with many metallic oxides with the production of hydroxides :—

$$CaO + H_2O = Ca(OH)_2$$

$$Na_2O + H_2O = 2NaOH.$$

Water converts some anhydrous salts into crystallo-hydrates, sometimes with change in the colour or in the crystalline structure of the anhydrous salt. Thus, *anhydrous* Copper sulphate is *white* in colour, but it turns *blue* when treated with water giving the *hydrated* salt. $CuSO_4, 5H_2O$.

Water *also* readily absorbs some gases forming unstable compounds :

$$NH_3 + H_2O = NH_4OH$$

$$SO_2 + H_2O = H_2SO_3$$

$$CO_2 + H_2O = H_2CO_3$$

On boiling, these compounds decompose and the gases are completely disengaged.

Water gas.—

When steam is passed over white-hot coke, a mixture of carbon monoxide and hydrogen, containing a little CO_2, is formed. The mixture is known as water gas.

$$H_2O + C = CO + H_2 \qquad 2H_2O + C = CO_2 + 2H_2$$

Tests for water.—

(1) A few drops of water are added to anhydrous copper sulphate. The colour of copper sulphate changes *from white to blue.*

(2) A few drops of water are added to a lump of freshly burnt quicklime. Much heat is generated and the lump of the lime falls to powder.

Purity of Water.—In general terms water is called pure when it is free from suspended and dissolved impurities, both organic and inorganic, solid, liquid or gaseous ; and is *free from all kinds of bacteria.*

Tests for pure water.—

The liquid—(i) must be colourless, tasteless and odourless ; (ii) shall freeze at 0°C ; (iii) shall boil at 100°C under 760 mm. presstre ; (iv) shall leave no residue on evaporation ; (v) must be neutral ; (vi) must not give a *precipitate* or *coloration* with—

(*a*) Silver nitrate solution (showing the absence of *chlorides*) ;

(*b*) Barium chloride solution (showing the absence of *sulphates* and *carbonates*) ;

(*c*) Nessler's solution (showing the absence of *ammonia* as such, or derived from nitrogenous organic compds., and nitrates, etc, by reduction) :

(*d*) Lime-water (showing the absence of CO_2, *Bi-carbonates of* Ca and Mg and *Carbonates*).

Volumetric Composition of Water

The volumetric composition of water (or steam) can be determined either analytically or synthetically :

(i) Analytical Method.

Electrolysis : Voltameter—Expt.—A glass basin containing two vertical platinum foils, fused into glass at its bottom, is half-filled with water. The water is slightly acidulated with H_2SO_4. Graduated tubes, filled with acidulated water are inverted over the platinum foils. The foils are now connected with the two ends of a battery and electric current is set on.

Observation.—Bubbles of gas from about the foils begin to rise into the tubes. It is found that after some time oxygen collects in the tube containing the *anode*, while hydrogen collects in the tube containing the *cathode*. That the gas liberated at the anode is oxygen is proved by the facts that it rekindles a glowing chip of wood, produces *brown* fumes with NO, and is completely absorbed by alkaline pyrogallate. That the other gas is hydrogen is proved by the fact that it burns in oxygen giving H_2O only. It is also found that the vol of oxygen liberated is *nearly half* of the vol. of hydrogen obtained.

Conclusion.—Thus it is seen that water is composed of 2 vols. of hydrogen and 1 vol. of oxygen.

(II) Synthetical Method.

Volumetric Composition of Steam—Hofmann's Method

Expt.—The apparatus consists of a U-shaped eudiometer tube one limb of which is closed and graduated. Near the closed end, two platinum wires are sealed into the glass for firing gases by a spark. The closed limb is surrounded by a wider tube which serves as a jacket (fig. 47). The other limb is open and is provided with a side-cock near the bottom. The closed limb is filled with mercury. A mixture of 2 volumes of hydrogen and 1 volume of oxygyn (*detonating gas* as obtained by the electrolysis of water), and *dired* by conc. H_2SO_4 is introduced into it by the displacement of mercury. Vapour of amyl alcohol, obtained by keeping the alcohol boiling (*boiling-point* 132°C) in a flask, is now passed through a tube at the top of the jacket and this continued up to the end of the experiment. Amyl-alcohol vapour passing out of the jacket by the lower tube is led to a condenser. After some time, when the temperature of the mixed gases becomes constant, the mercury in the two limbs is brought to the same level; and the volume of the mixtures is carefully noted. Some mercury is run out by means of the side-cock to reduce the pressure (otherwise the violence of the explosion may shatter the apparatus), the open end is closed by the thumb and electric spark is passed from an induction coil. Combination takes place between hydrogen and oxygen. Mercury is now added to bring it to the same level in both the limbs; and the volume is again measured.

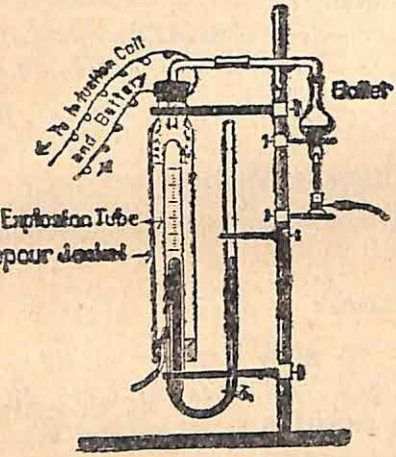


Fig. 47—Hofman's expt. on the Vol. Comp. of Steam

Observation.—It is found that the volume of steam produced is exactly *two thirds* of the vol. of the mixture of hydrogen and oxygen originally taken.

Conclusion.—Thus it is proved that 2 vols. of hydrogen combine with 1 vol. of oxygen to produce 2 volumes of steam.

Molecular formula of Steam (or Water) can be deduced from its volumetric composition.

Let one volume of oxygen contain n molecules.

Then 2 volumes of hydrogen as also two volumes of steam will contain each $2n$ molecules (by Avogadro). So from the volumetric composition of Steam, we can write,

$2n$ molecules of steam contain $2n$ molecules of hydrogen and n molecules of oxygen.

Or, 2 molecules of steam contain 2 molecules of hydrogen and 1 molecule of oxygen.

Or, 2 molecules of steam contain 4 atoms of hydrogen and 2 atoms of oxygen. (∵ hydrogen and oxygen molecules are diatomic)

Or, 1 molecule of steam contains 2 atoms of hydrogen and 1 atom of oxygen.

Hence, the molecular formula of steam (or water) is H_2O.

Gravimetric Composition of Water

(1) Dumas' method.—Hydrogen gas, prepared in Woulfe's bottle, is passed through a series of U-tubes containing lead nitrate solution, silver sulphate solution, KOH, conc. H_2SO_4 which absorb the impurities and moisture present in hydrogen. Thus *purified* and *dried*, hydrogen gas is now passed through a straight $CaCl_2$ tube *(drying tube)* attached to a *weighed* bulb-tube containing *dry* Cupric oxide. The other end of the bulb-tube is connected with a *weighed* U-tube containing fused $CaCl_2$ (fig. 48). After the gas has been passed for some time, so as to drive away the air from inside the whole apparatus, the bulb-tube is strongly heated. Hydrogen combines with the oxygen of copper oxide reducing it to metallic copper and producing water which is absorbed in the $CaCl_2$ U-tube.

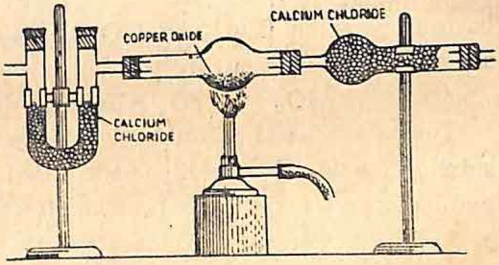


Fig. 48,—Gravimetric Comp. of water – Dumas' Expt.

$CuO + H_2 = Cu + H_2O$

After the experiment, the whole apparatus is cooled in the current of hydrogen ; and when quite cold, both the U-tube and the bulb-tube are detached and carefully weighed. The *gain* in the wt of calcium chloride U-tube gives the wt. of water formed and the *loss* in the wt. of the bulb-tube givess the wt. of oxygen that has combined with hydrogen to form that water.

Calculation.—Let the

$$\left.\begin{array}{ll}\text{wt. of bulb} + CuO \textit{ before reduction} & = w_1 \\ \text{wt. of bulb} + Cu + CuO \textit{ after reduction} & = w_2\end{array}\right\}$$

∴ wt. of $O = (w_1 - w_2)$

$$\left.\begin{array}{ll}\text{wt. of } CaCl_2 \text{ U-tube } \textit{after} \text{ expt.} & = w_3 \\ \text{wt. of } CaCl_2 \text{ U-tube } \textit{before} \text{ expt.} & = w_4\end{array}\right\}$$

∴ wt. of $H_2O = (w_3 - w_4)$

Hence, the wt. of hydrogen used up $= (w_3 - w_4) - (w_1 - w_2)$.

If the experiment be carefully performed, it will be found that

$$(w_1 - w_2) : (w_3 - w_4) = 8 : 9 \text{ and}$$

$$(w_1 - w_2) : \{(w_3 - w_4) - (w_1 - w_2)\} = 8 : 1.$$

That is to say, 8 parts by wt. of oxygen combine with 1 part by wt. of hydrogen to form 9 parts by wt. of water.

Hydrogen peroxide, H_2O_2

Occurrence : Hydrogen peroxide is formed during electrolysis of water and also as an intermediate product during combustion of hydrogen, but owing to the high temperature produced it undergoes immediate decomposition into water and oxygen. If a hydrogen flame is allowed to impinge on a piece of ice, traces of hydrogen peroxide can be detected in the water produced.

Preparation : It can be prepared by adding a paste of hydrated barium peroxide (BaO_2, $8H_2O$) to ice cold dilute sulphuric acid until the solution is only faintly acid.

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2.$$

Insoluble barium sulphate is now filtered off. The excess of sulphuric acid is carefully neutralised with a few drops of barium hydroxide and again filtered. The filtrate obtained is a dilute solution of hydrogen peroxide. Concentrated solution of hydrogen peroxide may be obtained by the distillation of the dilute solution under reduced pressure.

Phosphoric acid may also be used in place of sulphuric acid for the preparation of hydrogen peroxide. Phosphoric acid acts as a negative catalyst retarding the decomposition of hydrogen peroxide.

$$3BaO_2 + 2H_3PO_4 = Ba_3(PO_4)_2 + 3H_2O_2.$$

Properties : Hydrogen peroxide is a colourless liquid in a thin layer but has a bluish tinge in thick layer. When pure, it has a pungent odour like nitric acid. It is soluble in water.

It is unstable and decomposes liberating oxygen when heated or when brought in contact with a rough surface. MnO_2 or metals like Au, Pt, etc. $2H_2O_2 = 2H_2O + O_2$

It is an oxidising agent. It oxidises black lead sulphide into white lead sulphate. $PbS + 4H_2O_2 = PbSO_4 + 4H_2O$

It liberates iodine from potassium iodide

$$2KI + H_2O_2 = 2KOH + I_2.$$

In acid solution, instead of the alkali (KOH) a corresponding salt of the acid is produced.

$$2KI + H_2O_2 + 2HCl = 2KCl + 2H_2O + I_2$$

Hydrogen peroxide oxidises sulphurous acid (solution of SO_2 in water) into sulphuric acid.

$$H_2SO_3 + H_2O_2 = H_2SO_4 + H_2O$$

Sometimes, it acts as a reducing agent. It reduces ozone into ordinary oxygen. $O_3 + H_2O_2 = H_2O + 2O_2$

It also reduces acidified pot. permanganate causing an evolution of oxygen. The colour of the permanganate solution is discharged.

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$

N. B.—Strictly speaking, these are not examples of reduction, because the reducing agent (viz. H_2O_2) here is not oxidised, but is itself reduced.

Use.—Hydrogen peroxide is a bleaching agent. It is used for bleaching straw, feather, silk, hair, ivory etc. Solution of hydrogen peroxide is used in medicine and for restoring the colour of old oil paintings. It is also used as a laboratory reagent.

Test—(1) H_2O_2 liberates I_2 from KI solution even in presence of ferrous sulphate.

(2) It decolorises acidulated $KMnO_4$ solution.

(3) It turns a titanium salt orange yellow.

Exercise

1. What impurities are commonly present in ordinary water say river-water? Describe the experiment by which you have become aware of their presence. How would you proceed to prepare a sample of pure water from tap-water?
Cam. Jun. ; *Mad., 1937* . *Pat., 1929* ; *C. U., 1919.*

2. How will you determine the volumetric composition of steam? Give a sketch of the apparatus. *C. U., 1919, '47.*

3. How would you prove that water contains both hydrogen and oxygen? Give details of the experiments and a sketch of any apparatus you would use for the purpose. *C. U., 1919.*

4. Describe the process by which you would remove the dissolved solid matter in a sample of river-water. How would you account for the dtfferent behaviour of the water thus obtained with soap as compared with the original water? *C.U., 1914.*

5. Describe fully any experiment by which you determine the composition of water by weight, mentioning the precautions that you will take to get accurate results. Give the necessary calculations.
All., 1917 ; *Nag., 1929* ; *C. U., B. Sc. Hon, 1921, '29.*

6. What is the cause of hardness of water ? Are the following hard water or soft water ?—rain water, sea-water.

7. How would you test whether a given colourless liquid is or is not water ?
Rangoon ; *Cam. Jun.*, *1924.*

8. Explain 'Hard Water' with illustration. *Cal. Pre-U.*, *1964.*

9. What do you understand by hard water ? To what is hardness due ?
Describe any two methods for the removal of each type of hardness of water.
Cal. Pre-U., *1965.*

10. How is an aqueous solution of hydrogen peroxide prepared in the laboratory ? Describe with equations the action of hydrogen peroxide on (a) Potassium iodide, (b) Lead sulphide.
Describe two reactions where hydrogen peroxide behaves as a reducing agent.
Cal. Pre-U., *1965.*

11. How would you prepare a dilute aqueous solution of hydrogen peroxide ? How does hydrogen peroxide react with (a) Lead sulphide, (b) Potassium iodide, (c) Potassium permanganate solution acidified with dilute sulphuric acid ? Give equations. *Cal. Pre-U.*, *1967.*

12. What happens when hydrogen peroxide solution is added to acidified potassium iodide solution. *Cal. Pre-U.*, *1970*

CHAPTER XVI

NITROGEN AND ITS COMPOUNDS

Nitrogen

Symbol, N. Mol. formula, N_2. At. wt., 14. At. No., 7.

History.—Nitrogen was discovered in 1733 by Daniel Rutherford who called it mephitic (*poisonous*) air, for it did not support combustion or respiration. Lavoisier called it *azote.* The name nitrogen was suggested by Chaptal in 1790, for it is a constituent of nitre.

Occurrence—Nitrogen occurs in the free state in air and constitutes four-fifths of its volume. In combination, it is found in ammonia, nitre or potassium nitrate and Chilli saltpetre or sodium nitrate Nitrogen is an essential constituent of an important class of organic substances called the proteins. and is present in many other vegetable and animal products.

Modes of Formation of Nitrogen

1. **From Air.**—Nitrogen may be obtained from air by simply removing oxygen of the air by means of phosphorus, *strongly heated* copper, etc.

(*a*) *By means of Phosphorus.*—Take a porcelain crucible containing some white phosphorus and allow it to float on water in a trough.

Place a stoppered and *graduated* bell-jar over the crucible (fig. 49) and note the level of water in the jar. Now take out the stopper and ignite the phosphorus by touching it with a hot wire. Replace the stopper speedily. Phosphorus burns giving off dense white fumes of the pentoxide. $4P+5O_2 = 2P_2O_5$. At first the heat evolved expands the gas and depresses the water inside the jar. But after some time, the water begins to rise above the original level as P_2O_5 gradually dissolves in water. Ultimately water rises up and occupies $\frac{1}{5}$th of the volume occupied by air; the remaining $\frac{4}{5}$ths of that volume are occupied by nitrogen.

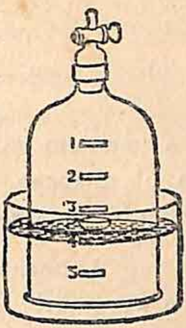


Fig. 49.—Preparation of Nitrogen from the air.

N. B —Nitrogen obtained from air by the removal of oxygen is not *pure*. It contains Argon, krypton, and other inactive gases of the atmosphere in *slight* traces.

This is the reason why the *density* of nitrogen as obtained from the air, is slightly *greater* than that of pure nitrogen prepared from its compounds. Pure nitrogen can *only* be obtained from compounds of nitrogen.

(*b*) *By means of heated copper.*—Pass air, freed from carbon dioxide through a hard glass tube containing pure copper turnings and heated to redness in a furnace. The oxygen of air combines with copper to form copper oxide and the gas that passes on is nitrogen. Collect the gas over water. $2Cu+O_2=2CuO$.

2. **From Compounds containing Nitrogen—**

(*a*) From *Ammonia*—Nitrogen can be obtained from ammonia by the action of chlorine (or bromine) on a concentrated solution of ammonia in water. Ammonia must be in *large excess*, otherwise nitrogen trichloride (NCl_3), a highly explosive compound, is formed when chlorine is passed into ammonia.

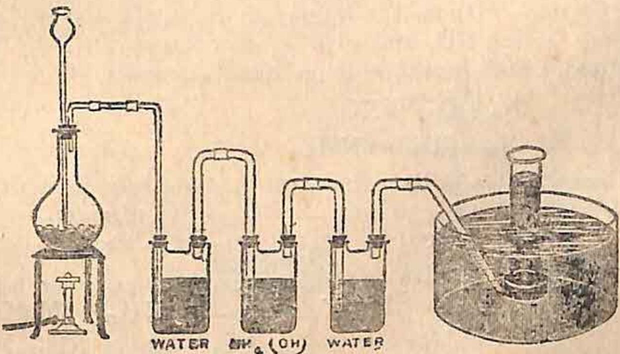


Fig. 50.—Preparation of Nitrogen from Ammonia by chlorine

$$2NH_3+3Cl_2=N_2+6HCl$$
$$6NH_3+6HCl=6NH_4Cl$$

Adding, $8NH_3+3Cl_2=N_2+6NH_4Cl.$

(*b*) By heating Ammonium nitrite

$$NH_4NO_2=N_2+2H_2O$$

Ammonium nitrite is unstable. Hence, in the laboratory preparation of nitrogen, it is produced in *Situ* by the interaction between sodium (or potassium) nitrite solution and ammonium chloride solution.

Laboratory method of Preparation of Nitrogen.

Take a mixture of concentrated solution of sodium or potassium nitrite and ammonium chloride in a small flask fitted with a thistle funnel and a delivery tube. See that the end of the thistle funnel always dips under the surface of the liquid in the flask. Heat the flask *gently*, and as soon as nitrogen containing a *little* NO, begins to be evolved, remove the source of heat. Pass the gas first through a *red-hot* tube containing copper turnings to reduce NO to nitrogen, and then through conc. H_2SO_4 and finally collect it over mercury. It is *pure* nitrogen.

$NH_4Cl+NaNO_2=NH_4NO_2+NaCl$ ‖ $NH_4NO_2=N_2+2H_2O$

Properties

Physical.—Nitrogen is a *colourless*, *odourless*, *tasteless* gas, *very little* soluble in water and slightly lighter than air. It is not poisonous ; but it cannot support respiration.

Chemical.—Nitrogen is inert or inactive *i.e.*, it does not readily combine with other elements. It is neither inflammable nor a supporter of combustion. Under the influence of electric sparks, it combines with oxygen giving NO, and with *excess* of oxygen NO_2 ; while with hydrogen (under high pressure) it produces ammonia.

$$N_2+O_2=2NO$$
$$N_2+3H_2=2NH_3$$

Elements like boron, silicon, calcium, magnesium, lithium, etc. unite with the gas, at red-heat, to form the respective *nitrides*.

$3Ca+N_2=Ca_3N_2$ ‖ $3Mg+N_2=Mg_3N_2$

On being treated with water, the nitrides decompose giving off ammonia.

$$Mg_3N_2+6H_2O=2NH_3+3Mg(OH)_2.$$

Nitrogen also combines with calcium carbide (CaC_2) at a high temp. giving calcium cyanamide which, with *superheated* steam, gives NH_3.

$CaC_2+N_2=CaCN_2+C$ ‖ $CaCN_2+3H_2O=CaCO_3+2NH_3$

Manufacture of Nitrogen.—It is obtained from Liquid Air. (See Page 118)

Test.—(1) It is a colourless gas and extinguishes a lighted taper. (2) It does not turn lime-water milky (*Cf.* CO_2). (3) It is absorbed by strongly heated magnesium. (4) It is not absorbed by strongly heated copper (*Cf.* oxygen),

Uses of Nitrogen.—It is used in the manufacture of NH_3, HNO_3, and some fertilizers ; for filling some electric bulbs, and for filling high-temperature thermometers.

Ammonia

Formula, NH_3. Mol. wt., 17. Density, 8·5

History.—Priestly prepared gaseous ammonia in 1775 by heating lime with sal-ammoniac. He called it '*alkaline air.*'

Occurrence.—Atmospheric air and natural waters contain small quantities of ammonia. It is produced in the slow natural decomposition of animal and vegetable bodies. The smell of ammonia can often be detected near stables and urinals. As nitrate it is found in rain-water, and as chloride and sulphate in the vicinity of volcanoes.

Source.—Ammonia is usually obtained from the (i) *ammoniacal liquor* of gas works ; (ii) by the destructive distillation of *nitrogenous organic matter* (horns, hoofs, bones, etc.) ; (iii) from *ammonium salts.*

1. **Preparation in the Laboratory.**—Ammonia may be obtained by heating almost *any ammonium salt* with *any alkali.*

In the Laboratory, it is usually prepared by heating a mixture of ammonium chloride (*sal ammoniac*) and powdered quicklime CaO or dry slaked-lime $Ca(OH)_2$.

$$2NH_4Cl + CaO = 2NH_3 + CaCl_2 + H_2O$$
$$2NH_4Cl + Ca(OH)_2 = 2NH_3 + CaCl_2 + 2H_2O.$$

Expt.—Mix dry powdered ammonium chloride with about *twice* its weight of *dry* slaked-lime in a mortar. Take the mixture in a hard glass test tube and clamp the test tube in a *slightly inclined* position to a retort stand (fig. 51). Leave a passage for the escape of the gas and heat the tube *carefully*. Ammonia is evolved. Pass it through a tower containing quick-lime and collect the *dry* gas by the downward displacement of air.

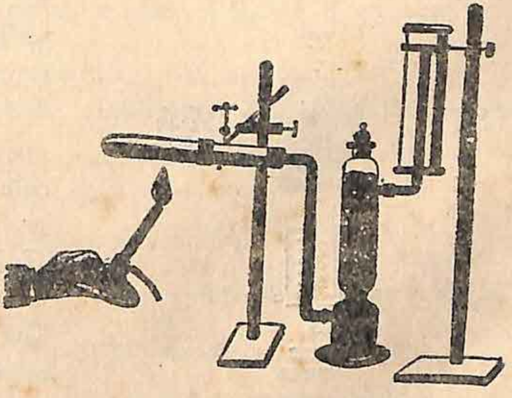


Fig. 51,—Preparation of Ammonia

Drying of Ammonia.—Ammonia is *best dried* by means of *quick-lime*. It cannot be dried by means of (*a*) *conc.* H_2SO_4, for it reacts with the acid producing ammonium sulphate; (*b*) *phosphorus pentoxide*, for it reacts with P_2O_5 and H_2O to yield ammonium phosphate; (*c*) *fused* $CaCl_2$, for the gas is absorbed by $CaCl_2$.

Collection of Ammonia.—Ammonia, being *highly soluble* in water, *cannot* be collected over water. It may be collected over mercury or by the *downward* displacement of air.

(2) Ammonia can also be obtained by reducing nitric acid, nitrites or nitrates with *nascent* hydrogen.

$$NaNO_3 + 8H = NaOH + 2H_2O + NH_3$$

$$NaNO_2 + 6H = NaOH + H_2O + NH_3.$$

(3) By the action of water of some metallic nitrides—

$$Mg_3N_2 + 6H_2O = 3Mg(OH)_2 + 2NH_3$$

Manufacture of Ammonia

1. **By product Ammonia.**—Ammonia is obtained as a by-product in the manufacture of coal gas. During the *destructive distillation* of coal for the manufacture of coal-gas, *ammoniacal liquor* is obtained as a *by product*. To get ammonia, the ammoniacal liquor is boiled with milk-of-lime; and the ammonia, that is evolved, is directly passed into water containing ice, till a very strong solution is produced. We then get *liquor ammonia* of commerce.

To get ammonium salts, the evolved ammonia, instead of being passed into water is absorbed either in hydrochloric acid, when we get ammonium chloride; or sulphuric acid, when it gives ammonium sulphate. These salts form a ready source of ammonia.

2. Haber's Synthetic Process of Manufacture of Ammonia

Details.—A mixture of *pure* nitrogen and *pure* hydrogen in the proportion of 1 : 3 by vol. is compressed under 200 atmospheres and then passed through a chamber heated to to 500°-550°C containing *finely divided* iron (which acts as a *catalytic agent*) mixed with a *promoter* like molybdenum. Hydrogen and nitrogen combine together to form NH_3. The issuing gases consisting of ammonia and uncombined nitrogen and hydrogen are *cooled* under pressure, when ammonia is liquefied, but not the other two gases. Liquid ammonia

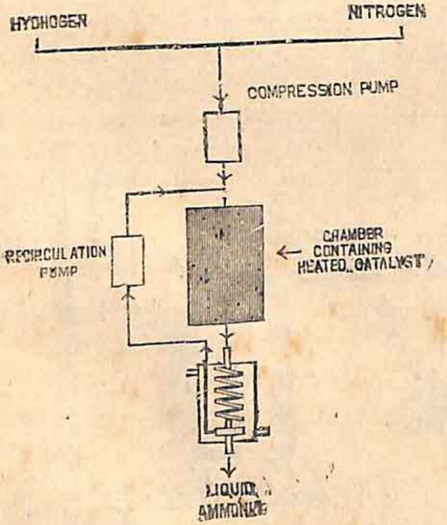


Fig- 52,—Haber's Process

is removed. The unconverted nitrogen and hydrogen mixed with fresh gases are *recirculated* under pressure, by means of pumps over the catalyst and converted into more ammonia (fig. 52).

$$N_2 + 3H_2 \rightleftharpoons 2NH_3.$$

Properties

Physical.—It is a *colourless* gas with a *very pungent* smell (bringing tears to the eyes) and an *alkaline* or *soapy taste*. It is lighter than air, and is exceedingly soluble in water. It can be easily liquefied..

The critical temp. is 132·5°C and the critical pressure is 112·3 atmos.

That ammonia gas is highly soluble in water and is alkaline in reaction can be demonstrated by means of a simple experimet known as fountain experiment.

A dry round bottomed flask is fitted up with a rubber cork and a glass tube ending in a jet inside the flask (fig. 53). It is completely filled with ammonia gas and then dipped in water coloured red with litmus. After sometime, the water is found to rush up into the flask in the form of a fountain. Also the colour of the liquid changes from red to blue. This expt. shows that ammonia gas is highly soluble in water and is alkaline in reaction.

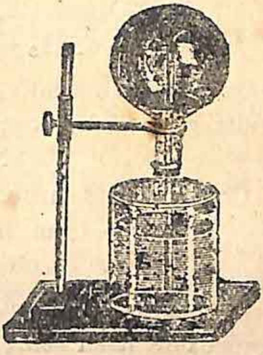


Fig. 53.—Fountain experiment

Chemical.—Ammonia does not support combustion nor does it burn in air. But in oxygen it burns with a yellowish flame, $4NH_3 + 3O_2 = 2N_2 + 6H_2O$. Mixtures of ammonia and oxygen are explosive. When NH_3 is passed over heated Na or K, we get the amide of Na or K and hydrogen.

$$2NH_3 + 2Na = 2NaNH_2 + H_2.$$

It is alkaline, turns *red* litmus solution *blue*, and neutralizes acids to form ammonium salts.

$$NH_3 + HCl = NH_4Cl \parallel NH_3 + HNO_3 = NH_4NO_3$$
$$2NH_3 + H_2SO_4 = (NH_4)_2SO_4.$$

The solution of ammonia in water reacts alkaline. Part of ammonia combines with water molecules to give ammonium hydroxide which in its turn dissociates to give ammonium (NH_4^+) ions and hydroxide (OH^-) ions.

$$NH_3 + H_2O = NH_4OH \parallel NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

A solution of ammonia in water, therefore, contains besides NH_3 and NH_4OH molecules, NH_4^+ (ammonium) and OH^- (hydroxide) ions. The solution smells of ammonia.

The strongest solution is called *liquor ammonia*. When this solution is boiled, ammonia is given off. Thus a ready supply of ammonia can be had by boiling commercial liquor ammonia and drying the issuing gas by means of quicklime.

Ammonium hydroxide precipitates the insoluble hydroxides (sometimes, the oxides) of many metals from the solutions of their salts. In a few cases, the precipitated hydroxides (or the oxides) dissolve in excess of ammonium hydroxide giving solutions of complex amines.

$$FeCl_3 + 3NH_4OH = \underset{\text{Brown Ppt.}}{Fe(OH)_3} + 3NH_4Cl$$

$$2AgNO_3 + 2NH_4OH = Ag_2O + H_2O + 2NH_4NO_3$$

$$Ag_2O + 4NH_3 + H_2O = 2\,[Ag(NH_3)_2]OH$$

Ammonia is partially decomposed by electric sparks giving a mixture of nitrogen and hydrogen.

$$2NH_3 \rightleftharpoons N_2 + 3H_2$$

Chlorine acts upon it to form hydrochloric acid and sets nitrogen free. HCl, thus formed, reacts with excess of NH_3 giving NH_4Cl.

$$8NH_3 + 3Cl_2 = N_2 + 6NH_4Cl.$$

Like hydrogen, ammonia is a reducing agent. It reduces red hot cupric oxide, itself being oxidised into nitrogen.

$$3CuO + 2NH_3 = 3Cu + 3H_2O + N_2$$

Test.—(1) It is a *pungent-smelling* gas which turns *red* litmus *blue*. (2) It produces *white fumes* in contact with hydrochloric acid gas. (3) It turns Nessler's solution *brown*. (N. B.—The presence of ammonia in *very minute quantities* is detected by Nessler's solution) and (4) it turns mercurous nitrate solution *black*.

Use.—Liquefied ammonia is used as a refrigerating agent, especially in the manufacture of ice. Aqueous ammonia is used as a cleansing agent (for it can dissolve grease) ; as a laboratory reagent ; and in medicine. Ammonia is also used in the manufacture of sodium carbonate by the Solvay's process ; and in the manufacture of ammonium salts.

Ammonium salts

Ammonia forms with acids a series of salts which resemble those of potassium and sodium in which the group NH_4, consisting of *one* atom of nitrogen and *four* atoms of hydrogen, plays the part of an atom of an element. It is called a Compound Radical (symbol, Am).

Def. of Compound Radical (or Radical).—A Compound Radical is a group of atoms of different elements which can pass into and out of compounds as a single unit (like an atom) without itself undergoing decomposition.

Examples.—The group NH_4 is one of the best examples of a compound radical. SO_3, SO_4, NO_3, CH_3, etc., are other examples of compound radicals.

Dissociation.—Most of the ammonium salts *dissociate* at high temperatures. Thus when ammonium chloride is heated, it splits up into ammonia and hydrochloric acid gas ; but on cooling, these two gases re-unite to give ammonium chloride back. This is dissociation. This action, is *reversible*, and is usually represented thus :

$$NH_4Cl \rightleftharpoons NH_3 + HCl.$$

Definition of Thermal (or Ordinary) Dissociation.

When the molecules of a substance break up on heating into simpler molecules or atoms which, on cooling re-unite to form the original molecules of the substance, the phenomenon is known as Dissociation, and the substance is said to dissociate.

Examples :

(i) Phosphorus pentachloride on heating breaks up into phosphorus trichloride and chlorine which recombine on cooling to give phosphorus pentachloride back.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

(ii) Calcium carbonate on strong heating breaks up into calcium oxide and CO_2. The products re-unite on cooling producing calcium carbonate again.

$$CaCO_3 \rightleftharpoons CaO + CO_2.$$

Nitric Acid, HNO_3

Nitric acid discovered by alchemists who called it aqua fortis because of its high solvent power.

Occurrence.—The acid occurs in small quantities in the atmosphere. It occurs in the solid as nitrate, the most important of which are saltpetre or nitre, KNO_3 and Chili saltpetre $NaNO_3$.

Preparation.—Nitric acid is a volatile acid. It is, therefore, expelled from its salts (a nitrate), by the action of a non-volatile acid like conc. H_2SO_4. This is also the principle for the preparation of other volatile acids *e.g.*, hydrochloric acid. Nitric acid is prepared in the laboratory by the action of conc. H_2SO_4 on potassium nitrate. The reaction takes place in two stages :

$KNO_3 + H_2SO_4 = KHSO_4 + HNO_3$ (1st stage—lower temp.)

$KHSO_4 + KNO_3 = K_2SO_4 + HNO_3$ (2nd stage—higher temp.)

The reaction is not pushed to the 2nd stage, for at the higher temperature

(*a*) a considerable amount of HNO_3 is decomposed and thereby lost.

(*b*) the acid may attack the material of the vessel.

Laboratory Method of Preparation.—Take *equal parts* by wt. of potassium nitrate and conc. sulphuric acid in a stoppered retort. Introduce the stem of the retort into a small flask floating on and kept cooled by water (fig. 54). Now heat the mixture, when Potassium nitrate reacts with sulphuric acid giving nitric acid which distils over and collects inside the flask. The residue in the retort consists chiefly of potassium hydrogen sulphate.

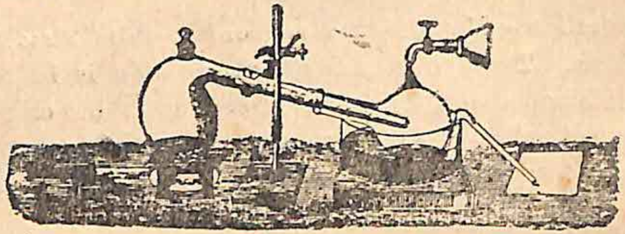


Fig. 54—Laboratory Method of Preparation of Nitric acid.

$$KNO_3 + H_2SO_4 = KHSO_4 + HNO_3$$

Manufacture (Industrial Preparation)—

Nitric acid can be manufactured by three different methods :

(1) From Chili saltpetre and conc. H_2SO_4.

(2) From ammonia by oxidation. (—Ostwald process)

(3) By the combination of nitrogen and oxygen of the air.
(—Arc process)

(1) **From Chili Saltpetre** and *conc.* H_2SO_4.—Nitric acid is manufactured by *distilling* a mixture of almost equal weights of Chili saltpetre and conc. H_2SO_4 in a cast-iron retort built in brick-work (fig. 55). The mixture is introduced through an opening at the top of the retort and its cover is replaced. The retort is now heated in the furnace, when nitric acid is produced.

The vapours of the acid escape through the outlet of the retort and condense first in a stone-ware Woulfe's bottle, and then in water-cooled stone-ware or silica pipes, yielding conc. HNO_3. The gases and vapours, which escape condensation, now pass up a tower, packed with stone-ware balls, down which cold water trickles. Here they dissolve in water giving dil. HNO_3.

The *acid sodium sulphate* is removed, in the liquid state, by means of a pipe at the bottom of the retort.

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3$$

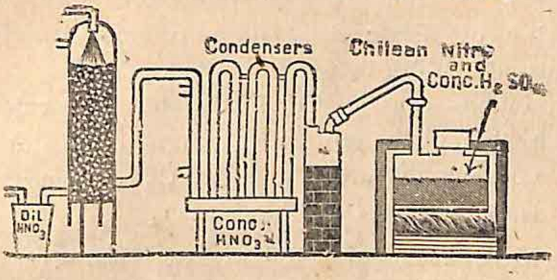


Fig. 55—Manufacture of Nitric Acid from Chili Saltpetre and conc. Sulphuric Acid.

(2) Nitric Acid from Ammonia (Ostwald process)—

Theory : When ammonia gas is burnt in oxygen, the products are N_2 and water. In presence of a catalyst (platinum), it is almost quantitatively oxidised by air into nitric oxide. The latter is then easily transformed into nitrogen dioxide with more air, which is then absorbed in water to form nitric acid.

The following conditions must be maintained :

(1) Ammonia must be pure and the air used to oxidise it must be free from dust particles.

(2) A catalyst (Pt) must be used.

(3) Time of contact with the catalyst must be short to avoid decomposition of NO produced into N_2 and O_2.

(4) Pressure : One atmosphere.

(5) Temperature : Between 700°C—800°C.

Details.—Ammonia gas mixed with air previously freed from dust particles etc. in proportion of 1 : 7·5 by volume is passed *rapidly* over platinum gauze at 700°—800°C. when ammonia is oxidised to nitric oxide which, with more oxygen forms nitrogen dioxide. Nitrogen dioxide is absorbed in water in a tower to form dilute nitric acid which is then concentrated by distillation with conc. H_2SO_4.

$$4NH_3 + 5O_2 = 6H_2O + 4NO$$
$$2NO + O_2 = 2NO_2$$
$$3NO_2 + H_2O = 2HNO_3 + NO$$

(3) Nitric Acid from the atmosphere (Birkeland and Eyde Electric Arc process)—

Purified air freed from CO_2 and moisture is passed through a thin electric arc (temp. 3000°C) when nitrogen and oxygen of the air combine to form some nitric oxide. The nitric oxide is cooled rapidly and converted into nitric acid in the same way as in the Ostwald process. This process is only possible where electricity is very cheap. It is now no longer used.

Commercial Nitric Acid.—The commercial acid is brown in colour, and contains chlorine, iodic acid, H_2SO_4, iron salts, N_2O_4, sodium sulphate, water, etc. as impurities.

Purification of Nitric Acid.—The commercial acid is purified by **fractionally distilling** it in glass retorts.

(1) 1st fraction—contains Cl_2, N_2O_4, etc. It is **rejected.**

(2) 2nd fraction or the **middle fraction is taken.** It

(i) does not give a ppt. with $AgNO_3$ solution ; but

(ii) it still contains water and N_2O_4.

Into the redistilled acid, while slightly warm, a stream of dry air or CO_2 is blown, till the liquid becomes colourless. The acid, now obtained, is pure acid and contains about 99·8% of the anhydrous acid.

(3) Residue left in the retort is rejected.

Properties

Physical.—Pure nitric acid is a *colourless, fuming, hygroscopic liquid* of specific gravity 1·52 at 14°C and boiling at 86°C with partial decomposition while 69 p.c. of the acid has a specific gravity of 1·43. It possesses a choking smell and a sour taste. It mixes with water in all proportions.

Chemical.—(1) Pure nitric acid decomposes to some extent when boiled under atmospheric pressure. At a higher temperature, it decomposes rapidly setting free oxygen and brown nitrogen dioxide gas.

$$4HNO_3 = 2H_2O + 4NO_2 + O_2$$

It is, therefore, a powerful oxidising agent. Conc. HNO_3 sets fire to dry and warm sawdust and straw. It oxidises black lead sulphide to lead sulphate, ferrous sulphate into ferric sulphate and liberates iodine from potassium iodide solution.

$$PbS + 8HNO_3 = PbSO_4 + 4H_2O + 8NO_2$$

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O$$

$$6KI + 8HNO_3 = 3I_2 + 6KNO_3 + 2NO + 4H_2O.$$

Action on Non metals.—

Nitric acid oxidises (1) carbon to carbon dioxide, (2) sulphur to sulphuric acid and (3) phosphorus to phosphoric acid.

1. **Carbon**—$[2HNO_3 = N_2O_5 + H_2O = N_2O_4 + H_2O + O \cdots\cdots (1)]$

$$4HNO_3 = 2N_2O_4 + 2H_2O + O_2 \ldots\ldots (1) \times 2$$

$$C + O_2 = CO_2$$

Adding, $C + 4HNO_3 = 2N_2O_4 + CO_2 + 2H_2O$

2. **Sulphur**—$2HNO_3 = N_2O_5 + H_2O = 2NO + H_2O + 3O$
$S + 3O = SO_3$
$SO_3 + H_2O = H_2SO_4$

Adding, $S + 2HNO_3 = H_2SO_4 + 2NO$

3. **Phosphorus**—$[2HNO_3 = NO_2 + NO + H_2O + 2O \ldots (1)]$
$10HNO_3 = 5NO_2 + 5NO + 5H_2O + 5O_2 \ldots\ldots (1) \times 5$
$4P + 5O_2 = 2P_2O_5.$
$2P_2O_5 + 6H_2O = 4H_3PO_4$

Adding, $4P + 10HNO_3 + H_2O = 4H_3PO_4 + 5NO_2 + 5NO$

Action on Organic Compounds.—

Nitric acid is highly corrosive and produces a painful wound when it comes in contact with skin. Feather, skin, silk, leather etc. are stained yellow by dilute nitric acid.

With glycerine, cotton etc. it forms highly explosive compounds (nitro-glycerine used for the manufacture of dynamite and gun cotton).

Action on Metals.—

Nitric acid attacks all metals except a few such as gold, platinum and iridium converting them into nitrates. Some metals (iron, aluminium etc.) do not dissolve in cold concentrated nitric acid, though they do so readily in dilute nitric acid. Treatment with highly concentrated nitric acid renders these metals *passive*, i.e. after treatment they do not dissolve even in dilute acids.

Unlike other acids, nitric acid does not liberate hydrogen when it reacts with metals except magnesium and manganese. Magnesium and manganese are the only two metals which with dilute nitric acid liberate hydrogen. $Mg + 2HNO_3 = Mg(NO_3)_2 + H_2$

There are several theories to account for the peculiar behaviour of nitric acid with metals.

According to one of these theories (oxidation theory), nitric acid first oxidises the metals into their oxides, which then dissolve in the acid to form the nitrates of the metal and water. At the same time nitric acid is reduced to one of these compounds.

$$HNO_3 \rightarrow NO_2 \rightarrow N_2O_3(HNO_2) \rightarrow NO \rightarrow N_2O \rightarrow N_2 \rightarrow NH_3$$

The extent of reduction suffered by nitric acid depends on many factors such as (1) the nature of the metal, (2) concentration of the acid and (3) temperature.

It is usually found that more dilute the acid, greater is the reduction. Thus, with concentrated HNO_3 the reduction product is invariably NO_2. With less active metals like copper, dilute nitric acid is usually reduced to NO, but with more active metals such as zinc, iron etc., reduction proceeds further, N_2O and if the acid is very dilute, NH_3 being produced. The latter compound (NH_3) is converted into ammonium nitrate in the presence of excess acid. Actions of HNO_3 on some typical metals are given below :—

Copper :

(1) *Cold* and *Conc.* HNO_3 with *Copper gives* NO_2

$2HNO_3=2NO_2+H_2O+O$

$Cu+O=CuO$

$CuO+2HNO_3=Cu(NO_3)_2+H_2O$

Adding, $Cu+4HNO_3=Cu(NO_3)_2+2H_2O+2NO_2$

(2) *Cold* HNO_3 *of moderate strength* gives NO

$2HNO_3=2NO+H_2O+3O$

$3Cu+3O=3CuO$

$3CuO+6HNO_3=3Cu(NO_3)_2+3H_2O$

Adding, $3Cu+8HNO_3=3Cu(NO_3)_2+4H_2O+2NO$

(3) HNO_3 *vapour passsed over Strongly heated Cu gives* N_2.

$2HNO_3=H_2O+N_2+5O$

$5Cu+5O=5CuO$

Adding, $5Cu+2HNO_3=5CuO+H_2O+N_2$

Zinc :

(1) *Conc* HNO_3 *with Zinc gives* NO_2,

$2HNO_3=2NO_2+H_2O+O$

$Zn+O=ZnO$

$ZnO+2HNO_3=Zn(NO_3)_2+H_2O$

Adding, $Zn+4HNO_3=Zn(NO_3)_2+2H_2O+2NO_2$

(2) *Cold and dil.* HNO_3 *gives with Zinc*, N_2O

$4Zn+4O=4ZnO$

$2HNO_3=N_2O+H_2O+4O$

$4ZnO+8HNO_3=4Zn(NO_3)_2+4H_2O$

Adding, $4Zn+10HNO_3=4Zn(NO_3)_2+5H_2O+N_2O$

(3) *Cold and very dil* HNO_3 *with Zinc gives* NH_4NO_3

$HNO_3+H_2O=NH_3+4O$

$4Zn+4O=4ZnO$

$4ZnO+8HNO_3=4Zn(NO_3)_2+4H_2O$

$NH_3+HNO_3=NH_4NO_3$

Adding, $4Zn+10HNO_3=4Zn(NO_3)_2+3H_2O+NH_4NO_3$.

According to another theory (Nascent hydrogen theory), nascent hydrogen is first liberated by the action of nitiric acid on a metal which then reduces the excess of acid to its various reduction products :— NO_2, N_2O_3, NO, N_2O, N_2 or NH_3. The exact nature of products depends on (1) the nature of the metal, (2) concentration of the acid and (3) temperature.

The *nascent* Hydrogen theory also enables us to write the equations conveniently. As before, we use *partial* equations. For example, *cold* and *dil*. HNO_3 dissolves iron giving ferrous nitrate and ammonium nitrate. We may assume that at first *nascent* hydrogen is produced.

$Fe+2HNO_3=Fe(NO_3)_2+2H$......(1)

This *nascent* hydrogen now reduces HNO_3 to give NH_3, which reacts with more HNO_3 to produce NH_4NO_3. Now to give NH_4NO_3, *nascent* hydrogen will not only *take away* all the atoms of oxygen from HNO_3 molecule, but must also *add* 3 atoms of hydrogen. That is to say, for 1 molecule of HNO_3 we require 8 atoms of *nascent* hydrogen. But Eq. (1) gives only 2 atoms of hydrogen. Hence to get 8 atoms, we multiply Eq. (1) by 4.

$$\begin{aligned} 4Fe+8HNO_3 &= 4Fe(NO_3)_2+8H \ldots\ldots (1)\times 4 \\ HNO_3+8H &= 3H_2O+NH_3 \\ NH_3+HNO_3 &= NH_4NO_3 \\ \hline \textit{Adding},\quad 4Fe+10HNO_3 &= 4Fe(NO_3)_2+NH_4NO_3+3H_2O \end{aligned}$$

Highly conc. HNO_3 renders iron *passive*. This point has been discussed already. With ordinary conc. HNO_3, NO_2 is given off and ferric nitrate is produced.

$$Fe+6HNO_3=Fe(NO_3)_3+3H_2O+3NO_2$$

Aqua Regia.—The noble metals such as gold and platinum are not acted upon by nitric acid of *any* strength, nor by hydrochloric acid. But they readily dissolve in a *mixture* of the two. The mixture of conc. HNO_3 and conc. HCl in the proportion of 1 : 3 is called *aqua regia* or *kingly water*, as it dissolves the king of metals, gold.

Its action is due to the fact that nitric acid oxidises hydrochloric acid setting free chlorine and forming nitrosyl chloride, NOCl. The latter compound also decomposes afterwards to yield more chlorine.

$$\begin{aligned} HNO_3+3HCl &= Cl_2+2H_2O+NOCl \\ 2NOCl &= 2NO+Cl_2 \end{aligned}$$

The chlorine liberated converts the metals into their chlorides which then go into solution as such. So when metals like gold dissolve in aqua regia, the chlorides and not nitrates are produced.

$$Au+3HCl+HNO_3=AuCl_3+NO+2H_2O$$

Test—(1) Add a drop of nitric acid to blue litmus solution. Litmus turns red. Hence HNO_3 is an acid.

(2) Add nitric acid to indigo solution. The colour is at once destroyed.

(3) Add a few drops of nitric acid to copper turnings taken in a test tube. Brown fumes are evolved and the solution turns blue.

(4) **Ring** test.—Take 2 or 3 drops of HNO_3 in a test tube and dilute the acid by completely filling the test tube with water. Take about 3 c. c. of this sol. in another test tube and add an equal vol. of conc. H_2SO_4 to it. Cool the mixture by dipping it in cold water for some time and, when *quite cold*, pour an equal vol. of freshly prepared $FeSO_4$ sol down the side of the test tube, when a *brown ring* is formed at the surface of contact of the two liquids (fig. 56)

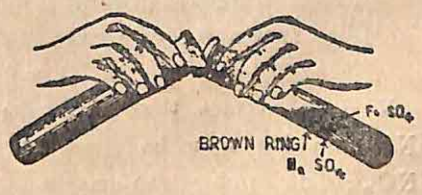


Fig. 56—Ring test for Nitric Acid.

Reactions.—Nitric acid oxidizes $FeSO_4$ in presenes of H_2SO_4 into $Fe_2(SO_4)_3$ and is itself *reduced* to NO. This NO dissolves in excess of $FeSO_4$ solution giving that brown coloured ring. ($NO+FeSO_4=FeSO_4, NO$)

$$2HNO_3+6FeSO_4+3H_2SO_4=3Fe_2(SO_4)_3+2NO+4H_2O.$$

Brucine test.—**Add a pinch of *brucine* to a drop or two of HNO_3 taken in a porcelain basin—a red colour is produced.**

Uses.—Nitric acid is used as a solvent for metals, for etching designs or names upon copper, brass and bronze articles ; in the manufacture of nitrates ; in the manufacture of sulphuric acid, dyes, explosives (like gun-cotton, picric acid, dynamite, etc.) ; in some electric cells ; and very dilute nitric acid is used is medicine.

To show that HNO_3 contains Nitrogen, Oxygen and Hydrogen.

(1) *HNO_3 contains Nitrogen.*

Pass HNO_3 vapour over heated Cu and collect the evolving gas over water. That the gas is N_2 is proved by the following tests ;

(i) It does not support combustion.
(ii) It does not turn lime water milky.
(iii) It is absorbed completely by Mg and not by Cu.

$$5Cu + 2HNO_3 = 5CuO + N_2 + H_2O.$$

(2) *HNO_3 contains Oxygen.*

Drop pure conc. HNO_3 over heated pumice stone and pass the issuing gas through a U-tube cooled in freezing mixture. Collect the gas coming out of the U-tube over water. That the gas collected is Oxygen is proved by the following tests :

(i) It rekindles a glowing chip of wood.
(ii) It produces brown fumes with NO.

$$4HNO_3 = 2H_2O + 4NO_2 + O_2$$

(3) *HNO_3 contains Hydrogen.*

Electrolyse the liquid collected in the U-tube in the above experiment after acidifying it with a drop of HNO_3. The gas which is evolved in the cathode is shown to be Hydrogen by the following tests :

(i) It burns with a blue flame.
(ii) The product of combustion does not turn lime water milky.
(iii) It is absorbed by heated Pd.

$$2H_2O = 2H_2 + O_2$$

N. B.—The fact that Hydrogen is evolved by the action of dilute HNO_3 on Mg may be cited as a proof for the presence of H_2 in HNO_3 ; but an objection may be raised against it, namely H_2 might have come from water and not from HNO_3.

Oxides of Nitrogen

There are *five* oxides of nitrogen :—

Nitrogen monoxide, *Nitrous oxide* or *Laughing gas*	N_2O
Nitric oxide	NO

Nitrogen trioxide, or *Nitrous anhydride*	N_2O_3
Nitrogen Dioxide, or *Nitrogen Tetroxide*	NO_2, N_2O_4
Nitrogen Pentoxide, or *Nitric anhydride*	N_2O_5

Nitrogen Monoxide or Nitrous Oxide

Formula, N_2O Mol. wt., 44 Density, 22

1. Laboratory Method of Preparation of Nitrous Oxide.—

Take *dry* ammonium nitrate (NH_4NO_3) in a flask fitted with a cork and a delivery tube. Heat the flask *gently*. Ammonium nitrate first melts and then decomposes into nitrous oxide and water.

$$NH_4NO_3 = N_2O + 2H_2O.$$

Collection.—As the gas is soluble in cold water, collect it by the displacement of *hot water*.

N.B.—Ammonium nitrate must not be heated strongly as at about 250°C it may decompose explosively. If nitrous acid is required dry, it is passed through conc. H_2SO_4 and then collected over dry mercury. Instead of ammonium nitrate, heat a mixture of ammonium sulphate and sodium nitrate when ammonium nitrate is produced as a result of double decomposition, which then decomposes as shown above to give N_2O.

$$(NH_4)_2SO_4 + 2NaNO_3 = Na_2SO_4 + 2NH_4NO_3$$
$$NH_4NO_3 = N_2O + 2H_2O$$

Properties

Physical.—Nitrous oxide is a *colourless* gas with a *faint smell.* When mixed with air and inhaled, it produces a kind of excitement accompanied by laughter. Hence, the name *laughing gas*. If the inhalation be long continued, it produces unconsciousness and insensibility to pain and may finally cause death. It is soluble in cold water and *four times more* in alcohol. The solution in water has a sweetish taste.

Chemical.—Like oxygen, nitrous oxide is not combustible, but it is a supporter of combustion. It rekindles a glowing chip of wood. Glowing charcoal and *feebly burning sulphur*, Mg, P, etc. *burn* as *brilliantly* in nitrous oxide as in oxygen. K and Na also burn brilliantly in the gas, when they are heated, giving the peroxides of the metals.

$$2N_2O + 2Na = Na_2O_2 + 2N_2$$

$$C + 2N_2O = CO_2 + 2N_2 \quad\Big|\quad S + 2N_2O = SO_2 + 2N_2$$
$$4P + 10N_2O = 2P_2O_5 + 10N_2 \quad\Big|\quad Mg + N_2O = MgO + N_2$$

It must be noted that the heat produced during the combustion of these substances decomposes the gas into nitrogen and oxygen ; and it is this oxygen that supports the combustion. If the heat produced is *not* sufficient to decompose the gas, then it *fails* to act as a supporter of combustion. Thus *feebly burning sulphur* is *extinguished* when introduced into a jar of N_2O, for the temp. is not sufficiently high to decompose N_2O. Strongly heated copper decomposes N_2O quantitatively. $N_2O + Cu = CuO + N_2$. It is a *neutral* gas and *does not* behave as hyponitrous anhydride.

Test.—(i) It rekindles a glowing chip of wood ; (ii) it *does not* produce brown fumes with nitric oxide ; and (iii) it does not react with alkaline pyrogallate giving a *brown* solution.

Nitrous oxide is distinguished from oxygen by tests (ii) and (iii) also by its faint odour (oxygen is odourless) and greater solubility in cold water and alcohol.

Use.—It is used in surgical operations as an anaesthetic.

Nitric Oxide

Formula, NO. Mol. wt. 30. Density, 15

Laboratory method of preparation of Nitric Oxide.—

Place some copper turnings in a Woulfe's bottle fitted with a thistle funnel and a delivery tube (fig. 33). See that the apparatus is air-tight (fig. 32). Now pour a mixture of equal volumes of conc. HNO_3 and water down the funnel, so that the end of the funnel dips below the surface of the liquid. Action at once sets in and nitric oxide is evloved *at the ordinary temperature* ; but the bottle is filled with brown fumes due to the reaction between nitric oxide and oxygen of the air inside the apparatus. Allow the gas to escape till the brown fumes are swept away.

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O,$$

Collection.—Now collect the gas over water.

Pure Nitric Oxide.—The gas, thus obtained, is more or less mixed with nitrogen, nitrous oxide and N_2O_4 as impurities. It is purified by passing it into a *cold, saturated solution* of $FeSO_4$. A *dark brown* liquid is obtained containing the compound $FeSO_4$, NO. The dark-brown solution, on being *heated*, yields *pure* NO.

Properties

Physical.—Nitric oxide is a *colourless* gas, insoluble in water, and slightly heavier than air.

Chemical.—*It is not combustible.* It does not decompose when *gently heated*, but it breaks up into nitrogen and oxygen at *high* temperatures. Consequently, nitric oxide *ordinarily does not support combustion* but does so at *high temperatures.* Thus a *lighted candle*, or *feebly burning* phosphorus, is extinguished in a jar of the gas. But when *vigorously burning* phosphorus is introduced, the gas is decomposed and phosphorus continues to burn in the oxygen *set free.*

$$4P+10NO=2P_2O_5+5N_2$$

Similarly, *feebly burning* sulphur is extinguished in nitric oxide; but if sulphur be *boiling*, when it is plunged into the gas, NO is decomposed and sulphur continues to burn in the oxygen set free. A mixture of nitric oxide and carbon disulphide-vapour, when ignited, burns with a brilliant bluish flash of light. In the above cases, *it is the evolved oxygen* that supports combustion.

It combines readily with free oxygen to form reddish-brown fumes of nitrogen dioxide, $2NO+O_2=2NO_2$.

Cold $FeSO_4$ solution freely absorbs NO giving a dark-brown solution of a substance having the composition $FeSO_4$, NO. This solution evolves NO when heated. $FeSO_4+NO \rightleftharpoons FeSO_4, NO$

Test.—(1) It is a colourless gas. (2) It forms reddish-brown fumes with the oxygen of the air.

Use.—It is used as an *Oxygen carrier* in the preparation of H_2SO_4 by the Chamber process.

Nitrogen trioxide or Nitrous Anhydride

Formula, N_2O_3. Mol. wt., 76 Density, 38.

Preparation.—(1) When a mixture of NO and NO_2 is passed through a tube cooled to about $-30°C$, a more or less impure form of nitrogen trioxide as a dark-blue liquid is obtained.

(2) It can be prepared by heating *gently* arsenious oxide (*white arsenic*) with *dil.* nitric acid (55% HNO_3) and leading the product into a *tube* kept immersed in a freezing mixture. N_2O_3 collects in the tube as a *deep-blue* liquid.

$$As_4O_6+4HNO_3=2As_2O_5+2H_2O+2N_2O_3,$$

Properties.—It is a reddish-brown gas at the ordinary temp. if dry. It dissociates with the rise of temp. $N_2O_3=NO+NO_2$. It reacts with ice-cold water giving nitrous acid. Hence it is called *nitrous anhydride.* It is completely absorbed by alkalis giving *nitrites.*

$$N_2O_3+H_2O=2HNO_2$$

$$N_2O_3+2KOH=2KNO_2+H_2O$$

Nitrous acid is unstable and is known only in the form of solution. Its salts, nitrites are, however, quite stable.

Nitrogen Dioxide and Tetroxide

Formula, NO_2 (*Nitrogen dioxide*) and
N_2O_4 (*Nitrogen tetroxide*)

Mol. wt., 46 and 92 Density, 23 and 46.

(1) It may be prepared by passing a mixture of nitric oxide and oxygen (2 : 1 by volume) slowly through a U-tube cooled in freezing mixture when it is obtained as a liquid.

$$2NO + O_2 = 2NO_2.$$

(2) Preparation in the Laboratory.—It may be prepared by strongly heating any metallic nitrate (except Na and K nitrates).

Experiment.—Take dry and powdered crystals of*lead nitrate in a hard glass test tube which is connected with a U-tube kept immersed in a freezing mixture (fig. 57). Heat the test tube carefully. Lead nitrate first melts and then decomposes into NO_2, PbO and oxygen. Nitrogen dioxide condenses at first as a greenish liquid and then as colourless crystals inside the U-tube. Oxygen escapes to the atmosphere, and lead monoxide is left in the test tube.

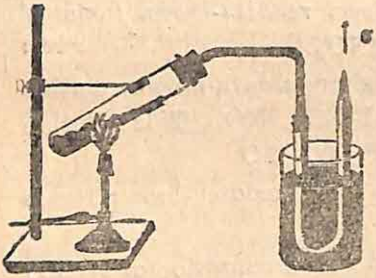


Fig. 57—Prep. of N_2O_4 from Lead nitrate.

$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2.$$

The gas may also be prepared by gently warming nitric acid with lumps of arsenious oxide and passing the issuing gases through a tube kept immersed in a freezing mixture.

Properties

Physical.—At low temperatures, nitrogen tetroxide is a colourless, crystalline solid which melts to a colourless liquid. At a temperature slightly above the melting-point, the liquid begins to acquire a pale-yellow colour which gradually deepens till it becomes orange. At the ordinary temperature nitrogen dioxide is a reddish-brown gas. As the temperature is raised, the colour becomes deeper till it is dark and opaque. On cooling, the reverse changes take place. This change in colour takes place due to dissociation of nitrogen tetroxide (colourless) producing deep brown nitrogen dioxide.

---

* Lead nitrate is preferred, for it does not contain water of crystallisation.

$$N_2O_4 \rightleftharpoons NO_2 + NO_2.$$

Nitrogen dioxide is poisonous, and has a suffocating odour.

Chemical—Gaseous nitrogen dioxide does not support the combustion of a lighted taper. Strongly burning phosphorus, carbon and sulphur, plunged into the gas, continue to burn with brilliancy, for the temp. of the burning substances is sufficiently high to decompose nitrogen dioxide with the evolution of oxygen.

Action of water.—Nitrogen dioxide is decomposed by water. If the temp. be *low* and the amount of water small, we get a mixture of nitric acid and nitrous acid.

$$N_2O_4 + H_2O = HNO_3 + HNO_2.$$

Since N_2O_4 gives, on being treated with water, both HNO_3 and HNO_2, it may be regarded as a mixed anhydride of both the acids.

At the *ordinary temperature*, with excess of water or with *hot* water, it gives nitric acid and NO.

$$3NO_2 + H_2O = 2HNO_3 + NO.$$

Nitrogen pentoxide

(Nitric Anhydride)

Formula, N_2O_5 Mol. wt., 108

It is the anhydride of nitric acid. It may be prepared by distilling a well-cooled mixture of nitric acid and P_2O_5 from a retort.

$$2HNO_3 + P_2O_5 = N_2O_5 + 2HPO_3$$

It is a white crystalline solid. With water, it gives nitric acid.

$$N_2O_5 + H_2O = 2HNO_3.$$

The Atmosphere

The atmosphere is the name applied to the gaseous mixture which envelops the earth and which is commonly called the 'Air'. The older chemists used the term 'air' in the same sense as we use the word 'gas'.

The atmosphere which is next to the surface of the earth is called troposphere. Above troposphere and extending for serveral hundred miles is the stratosphere. The exact extent of the stratosphere is uncertain, there being considerable disagreement between scientists in their estimates in this respect.

The air was thought to be an element by the early Greek and Hindu philosophers. It was the French chemist, Lavoisier who first discovered the real nature of air.

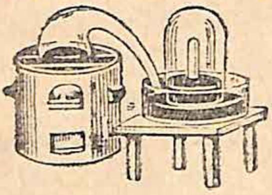


Fig. 58—Lavoisier's Expt.

In one of his historic experiments, Lavoisier took 4 ounces of pure mercury in a glass retort, the drawn out neck of which was communicated with a measured vol. of air inside a bell-jar inverted over mercury (fig. 58). The retort was heated in a furnace for 12 days to a temperature near the boiling-point of mercury and the changes were carefully noted. Red scales were seen floating upon the surface of mercury. The vol. of air inside the bell jar went on diminishing and mercury gradually rose up in it. After 12 days there was no further diminution in the vol. of air. Lavoisier measured the residual vol. of air, when cold, and compared it with the original. He found that the actual diminution in vol. was nearly equal to 1/5th of the vol of air originally taken.

The residual gas was not absorbed by hot mercury; it extinguished the flame of a burning candle; and a mouse was suffocated when placed in the gas. Lavoisier called it 'Azote' (*a*=no, *zoic* =life).

Lavoisier next performed the **reverse experiment.** He took the red scales and strongly heated them, when a gas was given off which Lavoisier collected in a graduated jar over mercury (fig. 59). The volume of the gas obtained was found to be equal to the diminution that took place when mercury was heated in the retort. This gas supported the combustion of a candle very energetically. Lavoisier first called this gas **'vital air'** and afterwards 'Oxygen'.

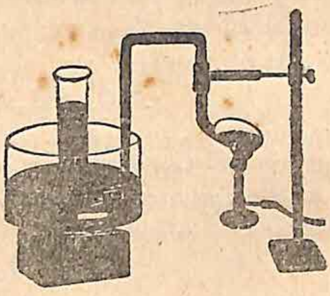


Fig. 59—Lavoisier's Expt.

Lavoisier thus proved that :—

(i) *The atmospheric air is made up of two gases ; Oxygen and Nitrogen* ; (ii) *the gases are of different nature* ; (iii) *one-fifth of the atmospheric air consists of* oxygen, *and the remainder is* nitrogen ; *and* (iv) oxygen *alone combines with the metals during calcination.*

Constituents of the Atmosphere—The air is principally a *mixture* of two gases oxygen and nitrogen, approximately in the proportion of *one* to *four* by *volume.*

21 per cent of Oxygen and 79 per cent of Nitrogen by Volume.

23 per cent of Oxygen and 77 per cent of Nitrogen by weight.

In addition to oxygen and nitrogen, there are other substances present in the air, in small quantities. The following is an average composition of the air by *volume.*—

Oxygen	20·60 vols.
Nitrogen	77·16 ,,
Water-vapour	1·40 ,,
Argon (Helium, Neon, Krypton, Xenon) ..	·80 ,,
Carbon dioxide	·04 ,,
	100·00 vols.

Ammonia, Hydrogen peroxide, Ozone, Nitric and Nitrous acids, Sulphur dioxide, Sulphuretted Hydrogen, etc. } *occur in traces*

Four Main Constituents of Air

(1) **Oxygen** supports respiration. It is thus a necessary article for animal life. We cannot live without Oxygen. Respiration results in the oxidation of some of the tissues in our system. It also purifies blood. Oxygen, again is absolutely necessary for all kinds of combustion on earth. It thus serves an important function in the economy of nature.

Detection ; (i) Expose a jar of NO tq air. Reddish brown fumes are produced which shows that air contains free oxygen.

(ii) Heat mercury to its near boiling point in air for a pretty long time when red scales are found to float on the surface of mercury. Collect these and heat them strongly when a gas is evolved which supports combustion more vigorously than air. The gas is absorbed completely in alkaline pyrogallate which proves that it is oxygen (see Lavoisier's Expt.)

(2) **Nitrogen** of the air *serves the important function* of diluting oxygen. If there were no nitrogen, then oxidation and combustion would be very rapid—dangerous for animal life.

Detection : Burn phosphorus in a closed volume of air over water. The gas left is nitrogen. It is colourless, non-inflammable and non-supporter of combustion. It is completely absorbed by heated Mg, but not by heated Cu.

(3) **Water vapour** checks to a certain extent the evaporating power of the atmosphere. It indirectly supports animal and vegetable lives, for it is by condensation of the water vapour that clouds are formed and ultimately the condensed water descends to the earth in the form of rain, snow, etc.

Detection : Put a lump of ice in a tumbler full of water and wait for sometime. Drops of water will be found to collect on the outside of the tumbler, evidently due to condensation of moisture present in air in contact with the cold surface.

(4) **Carbon dioxide** also plays an important role, as the plants with the help of sunlight breaks down the carbon dioxide of the atmosphere giving back the oxygen to the air. The carbon is retained by the plants which is converted by materials (water etc) derived from the soil through their roots to carbohydrates etc. The process is known as photosynthesis. The photosynthesis is important for animals as well, for the animals do not manufacture their own food, but depend for them on plants.

Through the respiration of animals (also of plants) and combustion of carbonaceous fuels, CO_2 in enormous quantities is continually being poured into the atmosphere. The process of photosynthesis serves to keep the percentage of CO_2 fairly constant and fit for breathing.

Detection : Take clear lime water in a shallow disk and expose it to air for sometime. The lime water will be found to be covered with a crust due to the formation of $CaCO_3$ by the action of CO_2 on lime water.

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O.$$

Air is a Mechanical Mixture and not a Chemical Compound.

The following facts prove that air is a *mixture* and not a compound :—

(1) When gases combine chemically, there is *always* a *thermal change*, and *often*, a *change in volume*. But when nitrogen and oxygen are mixed together in the proportion in which they are present in air, no change in volume or temp. takes place. The mixture behaves like ordinary air. Thus air is *not* a compound.

(2) A chemical compound is always formed by the combination of two or more elements in *definite* proportions by wt. This is not

the case with air ; for, though the proportion of nitrogen and oxygen in air by wt. is *nearly* constant, slight variations are observed in samples of air obtained from different localities. Even such a slight variation is not found with pure chemical compounds.

(3) Oxygen and nitrogen are not present in air in any simple multiple proportions of their atomic weights, which is necessary in all compounds.

(4) The relative density of air is 14·4 which corresponds with a mixture *roughly* of four vols. of nitrogen and one vol. of oxygen. If air were a compound, its formula would be N_4O *or more accurately*, $N_{15}O_4$ and its density would be 36 or 137 respectively. But its *actual* density is 14·4. Hence air is *not* a compound.

(5) The constituents of air *can* be separated by easy mechanical means. Thus nitrogen and oxygen present in the air can be separated :—

(*a*) *By diffusion.*—When air is passed through a porous tube, nitrogen, being lighter than oxygen, diffuses out more readily than oxygen. Had air been a chemical compound the constituent could not be separated in this way.

(*b*) *By vaporisation.*—When *liquid air* is allowed to evaporate, the more volatile nitrogen evaporates out first and the temp. of the liquid *rises*. If air were a chemical compound, liquid air would have evaporated *unchanged in composition* and at a *constant temp.*

(*c*) *By solution in water.*—Oxygen is more soluble in water than Nitrogen. Hence, when air is dissolved in water and the solution is heated to expel the *dissolved air*, it is found that the air, thus expelled, contains a greater percentage of oxygen than ordinary air. If air were a chemical compound, solution in water would not have altered its composition.

The Nitrogen Cycle

The inertness of ordinary nitrogen sometimes stands in the way to our realizing what important part this element plays in vegetable and animal metabolism. It forms one of the essential constituents of the class of substances known as **proteins** : and it is almost absolutely necessary for the maintenance of vegetable and animal lives. Plants, therefore, require nitrogenous food. The **never-exhausting** source of nitrogen is the air : and let us see how this source is tapped by Nature to supply nitrogenous food in the vegetable kingdom. That is to say, let us see how the atmospheric nitrogen is as is were fixed.

There are two ways by which this **Fixation of Nitrogen**, as the processes are called, takes place in nature. Some plants called the *leguminous plants* like peas, gram, etc. assimilate nitrogen directly from the air through the help of certain **bacteria** living in the nodules of their root-hair (fig. 60). The percentage of nitrogen thus *fixed* is very small as the number of leguminous plants is very small.

Majority of the plants, however, obtain nitrogen from *nitrogenous manures* present in the soil as nitrates, ammonium salts, etc. These nitrogenous salts in the soil are formed during the fixation of atmospheric nitrogen at the time of electric discharges, lightning, etc. in the air.

Electric discharges taking place in the air convert a portion of nitrogen into the oxides of nitrogen, which, with water, ultimately form nitric acid. The acid is carried down by rain into the soil to form nitrates with the bases present in the soil, and as stated above, is assimilated by plants.

Animals cannot assimilate nitrogen directly either from the air or from the soil. They are to depend upon nitrogenous plants which they eat and from which they derive their nitrogen, for the purpose.

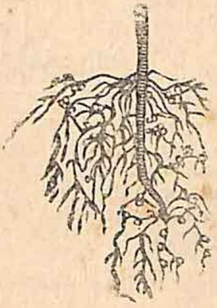
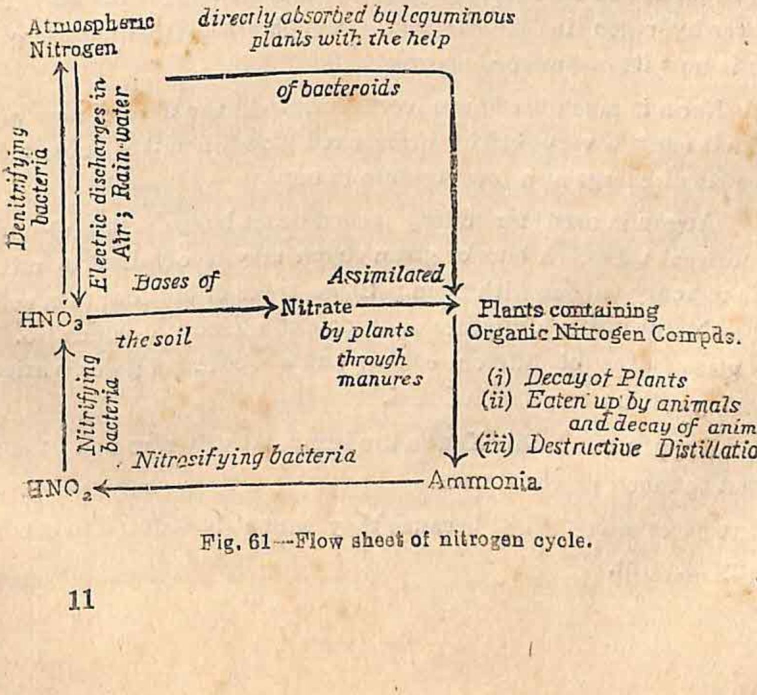


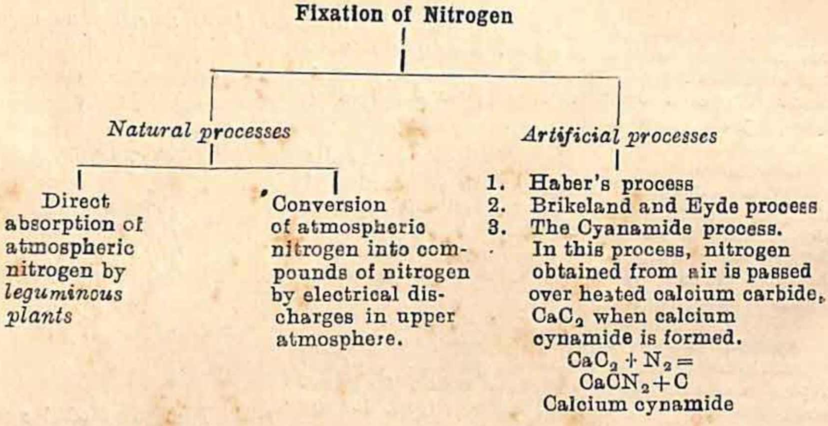
Fig. 60—Nodules in root-hair

When animals *die* and plants *decay* and putrefaction results, a small amount of nitrogen present in them goes back into the atmosphere, and the other portion of nitrogenous organic compound disintegrates and decomposes to produce *ammonia* which, by the help of **nitrosifying bacteria**, becomes converted into HNO_2, and finally, by nitrifying bacteria into HNO_3. Nitric acid now either passes into the soil *to form plant food* or is *converted by* **denitrifying bacteria** *into free nitrogen* for restoration to air. Thus the cycle of operation is complete, which keeps the amount of nitrogen in air nearly, but not exactly, constant.



Atmospheric Nitrogen
directly absorbed by leguminous plants with the help
of bacteroids
Denitrifying bacteria
Electric discharges in Air; Rain-water
Bases of
the soil
Assimilated
by plants
through manures
HNO3
Nitrate
Plants containing Organic Nitrogen Compds.
(i) Decay of Plants
(ii) Eaten up by animals and decay of animals
(iii) Destructive Distillation
Nitrifying bacteria
Nitrosifying bacteria
HNO2
Ammonia

Fig. 61—Flow sheet of nitrogen cycle.



Fixation of Nitrogen

Natural processes

- Direct absorption of atmospheric nitrogen by *leguminous plants*
- Conversion of atmospheric nitrogen into compounds of nitrogen by electrical discharges in upper atmosphere.

Artificial processes

1. Haber's process
2. Brikeland and Eyde process
3. The Cyanamide process.

In this process, nitrogen obtained from air is passed over heated calcium carbide, CaC_2 when calcium cynamide is formed.

$$CaC_2 + N_2 = CaCN_2 + C$$

Calcium cynamide

The Inert gases of the atmosphere

Nitrogen obtained from air was found to be a bit heavier than that derived from chemical compounds. This led Lord Raleigh in 1894 to suspect the presence of some unknown heavier inactive gases in the air.

A search for them ultimately led to the discovery of five **inert gases** given below.

(1) **Helium**—Pure helium is much lighter than air and is used for filling balloons and air-ships. Being non-inflammable, it has an advantage over hydrogen in this respect. It is obtained from natural gases which is now its commercial source.

(2) **Neon** is much used for advertisements in the form of *neon signs* because it emits a very bright orange red glow when it is subjected to an electric discharge at a low pressure (2 mm).

(3) **Argon** is used for filling incandescent lamps. It is also used in fluorescent tubes. A blue or green colour may be obtained by mixing a little mercury vapour with neon. Some types of blue or green colour may be obtained from a mixture of argon and mercury vapour also. By using glass tubes of different colours and a mixture of gases, varieties of pleasing colours may be produced.

(4) **Krypton** and (5) **Xenon** are comparatively rare and have not been put to much practical uses.

Inert gases are so called because they cannot be induced to combine with any element.

Exercise.

1. How may Nitrogen be obtained from (a) Air, (b) Ammonia and (c) Nitric Acid ? How would you proceed if you were to prepare a sample of *pure* Nitrogen and why ?
Cam. Jun. ; *C. U. 1921, '35* ; *All., 1923.*

2. Describe fully with diagram how to obtain pure Nitrogen from Potassium nitrate. What are the properties of this gas ?

3. How would you prepare *pure* and *dry* ammonia ? Describe one experiment each to demonstrate its solubility in water, inflammability, lightness and basic character.
Andhra U. ; *Pat. 1937* ; *Mad., 1930* ; *C. U., 1917, '20, '35, '46, Delhi. 1945.*

4. What is the action of Chlorine on Ammonia ? How would you make use of it to demonstrate that the formula of the gas is NH_3 ? What is *dissociation* ?
Lond. B. Sc. ; *C. U. I. Sc. 1936. '39* ; *B. Sc. 1916, '45*

5. (a) Is air a chemical compound ? Advance the reasons for your statement.

(b) What are the important gases present in air and in what proportions by weight and by volume ?
Cal. Pre U. 1970

6. How is Ammonia manufactured ? Distinguish between—(a) decomposition and dissociation, (b) gaseous and ionic dissociation.
Banaras ; *Bom., 1913* ; *C. U. 1932, '35, '37, 48.*

7. Sketch the apparatus you have actually used in the preparation of HNO_3. Describe the preparation and mention the principal properties of the compound. Starting with HNO_3, how will you prepare NO and NO_2 ?
Cam. Jun., 1925 ; *All., 1914* ; *Punj., 1915* ; *C. U., 1910, '35.*

8. Describe the effect of *conc.* HNO_3 on the leather, cotton, silver coin, gold-leaf, Zn, Cu, Hg ; and HNO_3 of *different* strengths on Zn, Mg, Cu, Sn, and Hg.
Banaras. 1935 ; *C. U. 1911, '14, '28, '31, '43, '54.*

9. How is pure Nitrous oxide prepared ? State its properties, compare its properties with those of oxygen.

10. How would you prepare *pure* Nitric oxide ? Describe its properties and tests. How will you determine its composition ?
C. U., 1914.

11. Describe how Nitric acid is obtained from the atmosphere. What is the effect of distilling (i) very pure and (ii) very dilute acid ? How will you obtain from it—(a) Oxygen, and (b) Ammonia.
Pat., 1928.

12. Demonstrate clearly that Nitric acid contains Nitrogen, Hydrogen and Oxygen.
Delhi. 1938 ; *Cam. Jun.* ; *Pat. 1926* ; *C. U., 1929.*

13. How does nature restore some of the Nitrogen compounds consumed by growing crops ?

14. Name the five *inactive gases* of the air. Why was their discovery so long delayed ? What are the uses of argon, helium and neon ?

15. Describe the laboratory method of preparation of Ammonia. State its important properties and uses.
Cal. Pre-U., 1961.

16. Give outlines of Haber's method for the manufacture of ammonia. State its properties and uses.
Cal. Pre U., 1962.

17. Describe how you would prepare nitric acid in the laboratory. Give a neat sketch of the apparatus. How will you obtain nitric acid from ammonia ? Describe with equations the action of nitric acid upon (a) metallic copper ; (b) sulphur.
Cal. Pre-U., 1963.

18. What are your arguments in favour of the statement 'Air is a mechanical mixture' ?

Describe suitable experiments to show the presence of (a) oxygen, (b) nitrogen and (c) carbon dioxide in air.
Cal. Pre-U., 1964.

19. How do you prepare *dry* ammonia in the laboratory? Describe its properties and uses. Give a neat sketch of the apparatus you would use. *Cal. Pre-U., 1964; '70.*

20. State with equation what would happen when ammonium nitrite solution is heated. *Cal. Pre-U. 1964.*

21. Describe briefly the manufacture of ammonia by Haber process.

State conditions necessary for conversion of ammonia to nitric acid on a large scale. *Cal. Pre-U, 1966*

22. What happens when ammonia gas is passed over heated copper oxide.? *Cal. Pre-U., 1967.*

CHAPTER XVII

HALOGENS AND THEIR COMPOUNDS

The four elements, fluorine, chlorine, bromine and iodine are called halogens because these elements, particularly the last three occur as constituents of sea salts, for example, Sodium Chloride (Hals = Sea salts, genas = produce).

They constitute one of the most well-defined groups (VIIB) of the periodic table bearing close resemblance to one another. Being situated in the extreme right of the periodic table, they represent elements of pronounced electronegativity, fluorine being the most electronegative of all the elements having the highest measure of non-metallic character. They have an outer-most shell of 7 electrons and so can attract one electron from other elements to complete their octet. Owing to their affinity for electrons they are oxidising agents (acceptors of electrons).

Many of the properties of halogens exhibit well-marked gradation, decreasing or increasing in a stepwise fashion from member to member. Flourine is a pale yellow gas, chlorine also a gas but denser than fluorine having a deeper greenish yellow colour, bromine a dark brown heavy liquid and iodine a grey crystalline solid giving violet vapours on heating.

Fluorine

Symbol. F. At. wt. 19. At. No. 9. Valency, 1.

Occurrence.—Fluorine is too active to occur in nature in the free state. It occurs chiefly as :—

(1) **Fluorspar** (or *Derbyshire spar*), CaF_2

(2) **Cryolite, AlF_3, $3NaF$.**

(3) **Fluor apatite, CaF_2, $3Ca_3(PO_4)_2$**

In small quantities Fluorine is found in bones, in the enamel of teeth, in oyster-shells, in plants, and also in certain mineral waters.

History.—Scheele in 1771 first obtained an acid which he called fluoric acid by heating fluorspar, CaF_2, with sulphuric acid. Davy in 1813 showed that it is a compound of hydrogen with a new element, which he named fiourine. Although the existence of fluorine was established beyond doubt, it defied all attempts at isolation for nearly seventy years. Davy tried to isolate fluorine by electrolysis of aqueous hydrofluoric acid, but got only hydrogen and oxygen and no new element.

Why all attempts at isolation of fluorine hitherto failed? (*Difficulties of isolation of Fluorine.*)

All attempts at isolation of fluorine hitherto failed for four reasons :—

(1) Powerful chemical activity of fluorine towards other elements.

(2) It attacked all the materials of the apparatus, whether made of glass, or carbon, etc. in which it was tried to be prepared.

(3) The method of electrolysis was **unavailable**, for on the one hand, solution of HF in water gave, on electrolysis, **hydrogen** and **oxygen** : while, on the other, *anhydrous* HF was a **non-conductor** of electricity.

(4) Exceedingly poisonous and corrosive character of anhydrous HF proved fatal to more than one chemist.

How Moissan overcame the difficulties and isolated fluorine in 1886.

(1) He used an apparatus made of an alloy of Pt and Ir which is less attacked by F_2 than Pt.

(2) He found that a solution of KHF_2 in anhydrous HF was a conductor of electricity unlike the latter alone and yielded fluorine on electrolysis.

Moissan's Method of Preparation—The apparatus consists of a U-tube, made of an alloy of platinum and iridium and provided with two side-tubes. It is fitted with stoppers made of *fluorspar* through which the electrodes, thickened at the ends and made of the *same* alloy, are introduced. The U-tube is filled with acid potassium fluoride dissolved in anhydrous hydrofluoric acid. (fig. 62). As the anhydrous acid is very volatile, the temp. is lowered to about −23°C by keeping the U-tube immersed in a bath of *methyl chloride* (b.-p. −23°C) which is constantly renewed from an iron cylinder acting as a reservoir. Electric

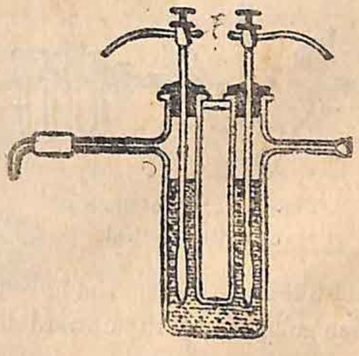


Fig. 62—Preparation of fluorine.

current is now passed, when hydrogen is liberated at the cathode, and fluorine at the anode. Fluorine passes out of the *side-tube.*

$$2KHF_2 = 2KF + H_2 + F_2$$

Fluorine, thus liberated but mixed with HF, is led *first* through spiral tube of platinum cooled to − 23°C by being kept immersed in methyl chloride (fig. 63). Most of the HF condenses in the spiral tube. The gas is then led through a platinum tube, packed with fused NaF, to remove the last trace of HF. Fluorine is now collected in a platinum vessel (for fluorine does not attack Pt at the ordinary temp.) by the upward displacement of air.

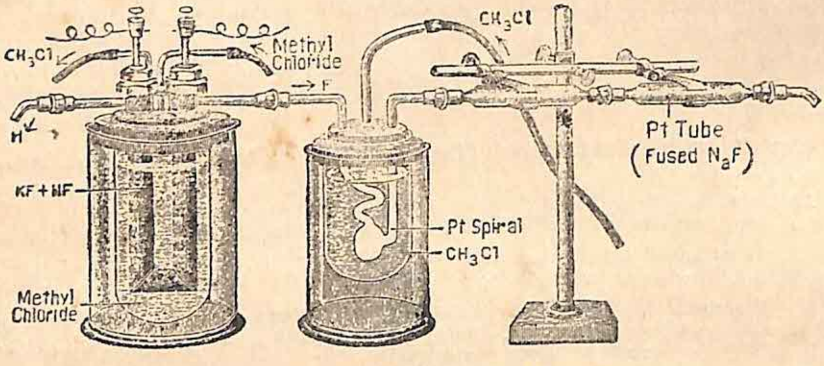


Fig. 63—Preparation of fluorine.

Recent method.—Fluorine is now prepared more easily by electrolysing fused potassium acid fluoride between graphite electrodes in a V shaped Copper vessels fitted with Copper caps through which graphite electrodes are introduced. (fig. 64). Fluorine which is set free at the anode is conducted through a series of U-tubes made of copper and filled with dry sodium fluoride to free the gas from HF. It is then collected by the upward displacement of air.

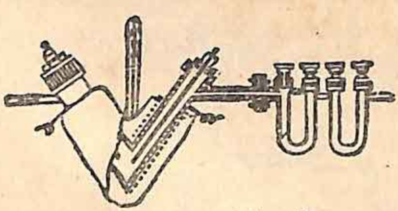


Fig. 64—Prep. of fluorine by recent method.

Properties

Physical—Fluorine is a pale greenish yellow gas. It possesses a peculiar penetrating odour and attacks the mucous membranes. It is heavier than air and liquefies at − 187°C and solidifies at − 233°C.

Chemical—It is the most chemically active element known. It combines with all elements, metals and non-metals directly except nitrogen, oxygen and inert gases. Some of the metals, such as sodium, potassium etc, and many non-metals, such as phosphorus, sulphur, carbon, bromine, iodine etc. burn spontaneously in the gas forming fluorides. $2Na + F_2 = 2NaF$ ‖ $C + 2F_2 = CF_4$

It decomposes water at the ordinary temperature liberating oxygen charged with ozone.

$$2F_2 + 2H_2O = 4HF + O_2 \quad \| \quad 3F_2 + 3H_2O = 6HF + O_3$$

Fluorine, being the most active of all the halogens, liberates chlorine, bromine and iodine from their respective compounds.

Fluorine reacts with aqueous alkalis to give fluorine monoxide

$$2NaOH + 2F_2 = 2NaF + F_2O + H_2O$$

Use : Fluorine is used now-a-days for the manufacture of certain hydrocarbon derivatives of fluorine for use (1) as lubricants capable of withstanding high temperature ; (2) as reagent-proof plastic (teflon) and (3) as refrigerants (freons).

Hydrofluoric acid (*Hydrogen fluoride*)

Formula, HF Density, 10

Occurrence—It does not occur free, but is found as salts in minerals like fluorspar, CaF_2 and cryolite (AlF_3, $3NaF$).

(1) Preparation of aqueous hydrofluoric acid.

It is prepared by warming powdered fluorspar with conc. H_2SO_4 in a lead retort and passing the evolved gas into water contained in lead bottles. It is marketted in guttapercha bottles.

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF$$

(2) Preparation of pure anhydrous hydrofluoric acid.

Pure anhydrous hydrofluoric acid is prepared by heating dry

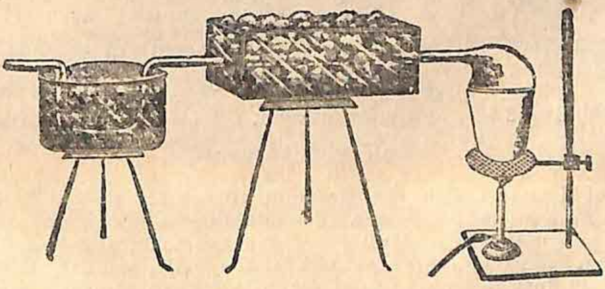


Fig. 65—Preparation of pure and anhydrous hydrofluoric acid.

pot. acid fluoride, KHF_2, (Fremy's salt) in a platinum retort joined to a platinum U-tube by means of a long tube of platinum. The platinum U-tube is cooled in freezing mixture in which anhydrous HF condenses to a liquid (fig. 65). $KHF_2 = KF + HF$

Potassium acid fluoride (Fremy's salt) is prepared by neutralising one half of the aqueous hydrofluoric acid by K_2CO_3 and adding the other half to it. The liquid is now evaporated to dryness.

$$K_2CO_3 + 2HF = 2KF + CO_2 + H_2O \quad \| \quad 2KF + 2HF = 2KHF_2$$

Properties

Physical—Anhydrous hydrofluoric acid is a *gas at the ordinary temp.* (in our country) which condenses to a *colourless fuming liquid* at 19·5°C. This liquid is very volatile, boils at 19·5°C and freezes at − 92°C. It is soluble in water. At 88°C and 741 mm. pressure the vapour density of hydrofluoric acid gas corresponds to HF. A few degrees above the boiling-point, the vapour density corresponds to H_3F_3.

Chemical—Hydrofluoric acid is a weak acid, nevertheless it dissolves all but noble metals evolving hydrogen.

$$2K + 2HF = 2KF + H_2$$

Though it is a weak acid, it is highly corrosive and poisonous. It causes deep wound when it comes in contact with skin and if inhaled, it may lead to permanent loss of voice.

It attacks silica and hence also glass which contains it.

$$SiO_2 + 4HF = \underset{\text{Silicon tetrafluoride}}{SiF_4} + 2H_2O$$

Use—The acid is very extensively used for *etching* glass.

Etching on glass—The glass article is first covered with a film of wax. The design to be etched, is now drawn on the waxed surface, and it is then *either* treated with HF sol. *or* exposed to the action of gaseous HF in a lead vessel (fig. 66). The glass is very soon etched. The wax is finally washed off with turpentine.

Fig. 66—Etching on glass

Fluorides of Metals : With the exception of fluorides of Na, K, NH_4 and Ag, the salts of HF are insoluble in water. The solubility of AgF in water distinguishes it from the corresponding salts of other halogen hydracids, namely AgCl, AgBr and AgI. Another noteworthy fact is that unlike $CaCl_2$ $CaBr_2$ and CaI_2, CaF_2 is soluble in water. Sodium fluoride is used as an insecticide in agriculture and for impregnating wood as a preservant.

Test for HF or Fluorides.

(1) Mix the fluoride with sand and heat the mixture with concentrated sulphuric acid. (If the heating is performed in a glass test tube, no sand need be added as the glass of the test tube contains sand). HF is evolved which reacts with the sand (SiO_2) to give silicon tetrafluoride, SiF_4. Hold a glas rod dipped in water over the issuing gas. The drop of water becomes opalescent due to the formation of *jelly-like* deposit of silicic acid.

$$\begin{aligned} CaF_2+H_2SO_4 &= CaSO_4+2HF \\ SiO_2+4HF &= SiF_4+2H_2O \\ 3SiF_4+4H_2O &= 2H_2SiF_6+H_4SiO_4 \\ &\quad \text{Hydrofluosilicic acid.} \end{aligned}$$

(2) Add $CaCl_2$ solution to the solution of a fluoride in water. A white ppt. of CaF_2, is obtained, which is insoluble in acetic acid.

Chlorine

Symbol, Cl. At. wt., 35·46 At. No., 1. Valency, 1.

Occurrence.—This element does not occur in nature in the free state. It is largely found, in combination with some metals, especially as *Common salt*, *Sylvine*, and *Carnallite*. In combination with Hydrogen it forms an important constituent of the gastric juice.

General Principle of Preparation—Chlorine is prepared—(1) from HCl *either* (*a*) by decomposition, *or* (*b*) by oxidation: (2) from a metallic chloride—*viz* HCl, or by decomposing the chloride by heat or electricity ; and (3) from a *hypochlorite* by a *dil.* acid.

(1) From HCl

(*a*) *By Decomposition.*—When a *strong* aqueous solution of HCl is electrolysed, we get hydrogen and chlorine. $2HCl=H_2+Cl_2$

(*b*) *By Oxidation.*—Chlorine can be obtained from HCl by *oxidizing* HCl by MnO_2, air, HNO_3, $KMnO_4$, $K_2Cr_2O_7$, etc.

Laboratory Method (*Schele's method*).—Take small lumps of manganese dioxide (pyrolusite) in a flask provided with a thistle funnel and a delivery tube and pour conc. HCl down the funnel so that it covers MnO_2 and the end of the funnel dips into the acid. A deep-brown solution is formed in the flask. The flask is gently heated on wire-gauze, when chlorine is evolved. Collect the gas by the *upward displacement of air*. (fig. 67)

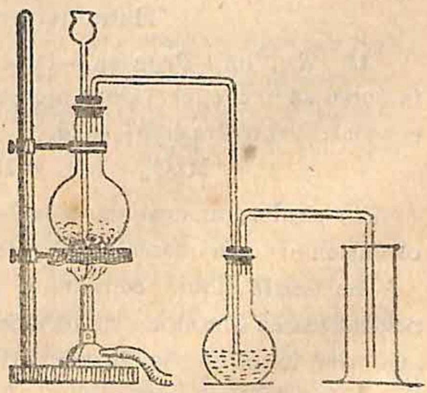


Fig. 67—Laboratory method of prep. of chlorine.

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2.$$

N. B. Chlorine gas as prepared above contains some unoxidised HCl. To free chlorine from HCl, pass the gas through a wash bottle containing water or through a U-tube packed with crystals of pot. permanganate. Water retains the more soluble HCl while pot. permanganate oxidises it into chlorine.

Chlorine may be prepared from HCl by oxidising it with other oxidising agents besides manganese dioxide, *e. g.*, $KMnO_4$, $K_2Cr_2O_7$, Pb_3O_4 (red lead).

From HCl and $KMnO_4$.—Take crystals of $KMnO_4$ (potassium permanganate) in a conical flask fitted with a dropping funnel and a delivery tube (fig. 40). Drop conc. HCl on $KMnO_4$ from the funnel when chlorine is given off, without heating.

$$2KMnO_4 + 16HCl = 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2.$$

(2) From a Chloride, conc. H_2SO_4 and MnO_2.—

Heat a mixture of metallic chloride, say NaCl, conc. H_2SO_4 and MnO_2 in a flask as in fig. 67. H_2SO_4 liberates HCl from the chloride. HCl, thus liberated, is now oxidised by MnO_2 with the evolution of Chlorine. Collect the gas as above.

$$2NaCl + 3H_2SO_4 + MnO_2 = 2NaHSO_4 + MnSO_4 + 2H_2O + Cl_2.$$

(3) From a hypochlorite—bleaching powder.—

Chlorine is evolved when bleaching powder is treated with dilute HCl or dilute H_2SO_4.

$$Ca(OCl)Cl + 2HCl = CaCl_2 + H_2O + Cl_2$$

Manufacture of Chlorine

(1) Weldon's Process.—In the Weldon process, chlorine is manufactured as in the laboratory process by heating manganese dioxide and concentrated hydrochloric acid.

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2.$$

The used up manganese dioxide is however, recovered and used for oxidation of fresh quantity of hydrochloric acid.

The waste liquid containing $MnCl_2$, HCl, iron salts etc. is first neutralised by limestone which after filtration to remove iron hydroxide and other impurities is treated with hot milk of lime and the precipitated $Mn(OH)_2$ is oxidised by passing compressed air, when a thin black mud (Weldon mud) having the composition CaO, MnO_2 ; CaO, $2MnO_2$ separates out. This is used again.

$$MnCl_2 + Ca(OH)_2 = Mn(OH)_2 + CaCl_2$$

$$2Mn(OH)_2 + 2Ca(OH)_2 + O_2 = \underset{\text{Weldon Mud}}{2CaO, MnO_2} + 4H_2O.$$

(2) **Deacon's Process.**—This process employs atmospheric oxygen to oxidize HCl. It depends upon the fact that when a mixture of HCl-gas and air (or oxygen) is heated, a *very* small amount of chlorine is evolved. $4HCl + O_2 = 2H_2O + 2Cl_2$. The reaction is greatly accelerated by the presence of a catalytic agent like cupric chloride, at the temp. of 450°C.

Both Weldon and Deacon's process are now obsolete.

(3) **Modern electrolytic process.**—Now-a-days, practically the whole of chlorine of commerce is obtained as a by-product in the manufacture of caustic soda by the electrolysis of brine (a strong solution of sodium chloride). Sodium chloride solution contains Na^+ ion, Cl^- ion as well as H^+ ion and OH^- ion derived from water. On electrolysis H^+ ion and Cl^- ion are preferentially discharged at the cathode and anode respectively. Na^+ ion and OH^- ion accumulate in solution, by the evaporation of which solid caustic soda is obtained. Chlorine together with hydrogen is obtained as by-products. Provision must be made so that chlorine does not come in contact with caustic soda.

This condition is secured in diaphragm cells (Nelson Cell) or mercury cathode cell (Castner Kellner Cell). For more details, see manufacture of caustic soda.

Properties

Physical.—Chlorine is a *greenish-yellow* gas, heavier than air and possesses a peculiar *irritating smell.* It is *poisonous* and attacks the mucous membranes. It can be easily liquefied. It is moderately soluble in water, but is *very slightly* soluble *in brine.* Hence it can be collected over *brine.*

Chlorine is liquefied by cold and pressure to an amber-yellow liquid (b. p. –34·5°C). Its critical temp. is 140·9°C, and critical pressure 76·1 atmos.

Chemical.—Chlorine *does not* burn, but, *like oxygen*, supports the combustion of *hydrogen*, *antimony*, *phosphorus*, *sodium*, *copper*, and many other substances, always with the formation of their *chlorides.*

It has got a very great affinity for hydrogen. A burning jet of hydrogen burns in a jar of chlorine with a greenish flame giving off fumes of HCl. (Fig. 68). $H_2 + Cl_2 = 2HCl$.

It not only readily combines with free hydrogen, but also with the hydrogen present in many compounds (especially the hydrocarbons).

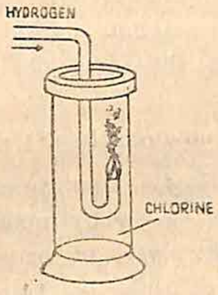


Fig. 68—Hydrogen burning in Chlorine.

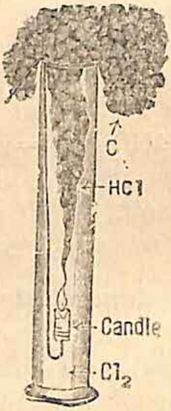


Fig. 69—A Candle burning in Chlorine.

A lighted paraffin candle when introduced into a jar full of chlorine burns with a dull-red smoky flame (Fig. 69). Chlorine combines with the hydrogen of the paraffin (C_xH_y) setting free HCl and black clouds of carbon are given off. Chlorine has little affinity for carbon.

$$C_xH_y + \frac{y}{2} Cl_2 = xC + yHCl.$$

When powdered antimony or arsenic is sprinkled into a jar of chlorine, each particle, as it falls into the jar burns with a bright spark producing fumes of $SbCl_5$ or $AsCl_3$.

$$2Sb + 5Cl_2 = 2SbCl_5$$
$$2As + 3Cl_2 = 2AsCl_3$$

A piece of phosphorus placed on a deflgrating spoon when introduced into a jar of chlorine first melts and then burns forming phosphorus tri-and pentachlorides.

$$4P + 6Cl_2 = 4PCl_3 \parallel 4P + 10Cl_2 = 4PCl_5.$$

Chlorine possesses bleaching properties. It can bleach vegetable colouring matters in presence of moisture.

Action of Chlorine on Water.—(i) When chlorine is passed into *water, cooled in ice*, we get a crystalline compound called *chlorine hydrate* ($Cl_2, 10H_2O$).

(ii) At the ordinary temp, chlorine dissolves in water giving a solution of the gas in water called *chlorine-water*.

(iii) It is *probable* that a cold aqueous solution of chlorine in water decomposes, forming a mixture of hypochlorous acid and hydrochloric acid. $Cl_2 + H_2O = HCl + HOCl$.

(iv) Chlorine-water cannot be preserved for a long time, as chlorine combines with hydrogen of water (especially in presence of sunlight) giving hydrochloric acid and oxygen.

Experiment.—Expose Chlorine-water to *bright sunlight.* The water is decomposed and bubbles of oxygen are evolved. $2Cl_2 + 2H_2O = 4HCl + O_2$ (fig. 70). Therefore old samples of Chlorine water turn *blue* litmus *red.*

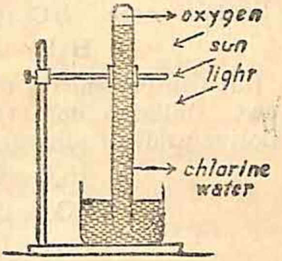


Fig. 70—Chlorine water in sunlight gives HCl and O_2

(v) Chlorine also reacts with *steam* giving HCl and oxygen.

Action of Chlorine on Alkalis.—When chlorine is passed into *cold* and *dilute solution* of caustic soda or caustic potash so that *excess of the alkali remains*, we get a mixture of the *chloride* and the *hypochlorite.*

$$Cl_2 + H_2O = HCl + HOCl \quad ..(1)$$
$$HCl + KOH = KCl + H_2O \quad ..(2)$$
$$HOCl + KOH = KOCl + H_2O \quad ..(3)$$

$$\text{Adding, } Cl_2 + 2KOH = KOCl + H_2O + KCl \quad ..(4)$$

But, if *excess* of chlorine is passed into *hot* solution of caustic soda or caustic potash, the hypochlorite that is formed in cold (eq. 4). is decomposed into the chlorate, and hence we get a mixture of the *chloride* and the *chlorate.*

$3KOCl = KClO_3 + 2KCl$ ... (5). Multiplying eq. (4) by (3) and adding (5), we get,

$$3Cl_2 + 6KOH = KClO_3 + 5KCl + 3H_2O.$$

Similarly, when chlorine is passed into *lime water*, or into *cold* and *dilute calcium* hydroxide solution so that excess of the alkali remains, *Calcium chloride and calcium hypochlorite* are obtained : whereas *hot milk-of-lime* treated with excess of chlorine yields *calcium chlorate* and *calcium chloride ;* and in the third place, chlorine passed over dry *slaked lime* at *about* 40°C gives *bleaching powder*, $Ca(OCl)Cl$.

$$2Ca(OH)_2 + 2Cl_2 = Ca(OCl)_2 + CaCl_2 + 2H_2O \text{ (in \textit{cold})}$$
$$6Ca(OH)_2 + 6Cl_2 = Ca(ClO_3)_2 + 5CaCl_2 + 6H_2O \text{ (when \textit{heated})}$$
$$Ca(OH)_2 + Cl_2 = Ca(OCl)Cl + H_2O$$

Oxidising action of Chlorine.—Chlorine acts as a strong oxidising agent.

(i) By directly combining with *i.e.* adding chlorine to a substance : thus ferrous chloride is oxidised by chlorine into ferric chloride.

$$2FeCl_2 + Cl_2 = 2FeCl_3 \;;$$

(ii) by removing hydrogen ; thus sulphuretted hydrogen is oxidised into sulphur by chlorine.

Pass H_2S gas into chlorine water or chlorine gas into a solution of H_2S in water. HCl is formed and sulphur is precipitated.

$$H_2S + Cl_2 = 2HCl + S.$$

(iii) In presence of moisture by actually adding oxygen to a substance. Chlorine here reacts with water to set free nascent oxygen. Chlorine oxidises sulphur dioxide solution into sulphuric acid.

$$\begin{aligned} H_2O + Cl_2 &= 2HCl + O \\ SO_2 + O &= SO_3 \\ SO_3 + H_2O &= H_2SO_4 \\ \hline SO_2 + Cl_2 + 2H_2O &= H_2SO_4 + 2HCl \end{aligned}$$

Chlorine also liberates bromine and iodine from bromides and iodides respectively. $2KBr + Cl_2 = 2KCl + Br_2 \parallel 2KI + Cl_2 = 2KCl + I_2$.

Another example of the oxidising action of chlorine is furnished by the *bleaching* properties it possesses.

Bleaching Action of Chlorine.—Introduce into several jars containing dry chlorine, one in each jar a *dry green leaf*, *dry red flower*, a piece of *red cloth*, a piece of *printed paper* brushed over with *writing ink* and then *dried*, or carrying black lead pencil marks. Notice that none of the materials shows any sign of bleaching. Now introduce a little water into each jar so as to moisten the articles. It is found that all the articles have been *bleached*, *excepting* the print and the pencil marks which remain unchanged.

We learn therefore, that—(1) *dry* chlorine cannot bleach *dry* colouring matters : (2) moisture is absolutely necessary for the purpose ; for chlorine combines with hydrogen of the moisture liberating oxygen in the *nascent* state, which *nascent oxygen* actually bleaches the colouring substance ; (3) consequently, chlorine *bleaches* by *oxidation* ; and (4) chlorine can decolourize writing ink but not *printer's* ink or lead pencil marks, for printer's ink and lead pencil contain carbon which is not acted upon by chlorine.

Test.—(1) Chlorine can be detected by its characteristic *greenish-yellow colour*, *peculiar odour*, and *bleaching properties*. (2) It liberates iodine from potassium iodide which (iodine) produces a blue colouration with starch sol. Hence chlorine can also be detected by iodized starch-paper.

Use.—Chlorine is used in the manufacture of bleaching powder, chloroform, bromine, chlorates, stannic chloride, etc ; as a disinfectant ; for preparing pure HCl and some *'poison gases'* like *phosgene gas, mustard gas*, etc. ; in the extraction of gold ; for bleaching purposes ; and for refining petroleum.

Hydrochloric Acid

(*Hydrogen chloride, Muriatic acid, Spirits of salts.*)

Formula, HCl. Mol wt. 36'5 Density, 18'25

History.—Mixture of HCl and HNO_3, called *aqua regia* was known to the Arabian Chemists about the 8th century. HCl was first prepared by Priestley.

Occurrence.—Hydrogen chloride is occasionally found in the gases emitted from volcanoes. It is also present in gastric juice. The salts of the acid occur plentifully in nature.

Laboratory method of Preparation—In the laboratory HCl is prepared by treating sodium chloride with conc. H_2SO_4. The reaction takes place in two stages. At first HCl and sodium hydrogen sulphate are formed, the latter, at a red heat, reacts with more sodium chloride producing normal sodium sulphate and more HCl.

$NaCl + H_2SO_4 = NaHSO_4 + HCl$ (*ordinary temp*, and *on gently heating*)

$NaHSO_4 + NaCl = Na_2SO_4 + HCl$ (*at a red heat*),

Experiment.—Take some common salt (NaCl) in a flask provided with a thistle funnel and a delivery tube. Pour conc. H_2SO_4 down the thistle funnel till it just covers the salt and the end of the funnel dips in the acid. A rapid stream of HCl-gas is given off, and in order to maintain a flow of the gas, *gently warm* the flask towards the end. Pass the gas through a wash bottle containing conc. H_2SO_4 and collect it by the upward displacement of air. As the acid is *highly soluble in* water, it cannot be collected over water. It can be collected over mercury.

Preparation of aqueous Hydrochloric acid—HCl gas is called *hydrogen chloride* to distinguish it from a solution of hydrochloric acid in water which is commonly called hydrochloric acid. The aqueous solution may be conveniently prepared in the laboratory by

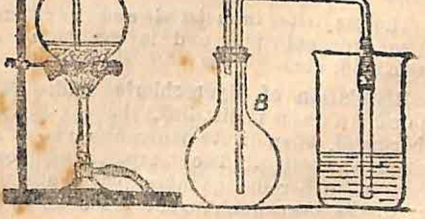


Fig. 71—Prep. of Aq. HCl with anti-suction device.

generating the acid in a flask (A), as described above and passing the issuing gas first through an *empty* flask (B) and then into water (fig. 71) The hydrogen chloride is absorbed by the water, and if the process be continued long enough, the solution finally becomes saturated. We get *concentrated* hydrochloric acid.

Antisuction Device.—An empty vessel is interposed between the generating flask and the vessel in which hydrochloric acid is absorbed in order to prevent water being sucked back into the generating flask due to great solubility of hydrochloric acid gas and causing serious accident by coming in contact with hot conc. sulphuric acid. The same purpose may be served by attaching an inverted funnel to the end of the delivery tube, so that the rim of the funnel may just touch the surface of the water (fig. 72).

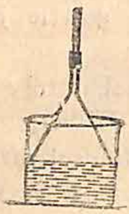


Fig. 72 —Antisuction device

Manufacture—(1) Hydrochloric acid is obtained in large quantities as a by-product during the manufacture of sodium carbonate by the Leblanc process. The gas is passed by towers, filled with coke, over which a slow stream of water flows. HCl acid gas dissolves in water, and we get hydrochloric acid of commerce (*See sodium*).

(2) Large quantities of hydrogen and chlorine obtained as by-products in the manufacture of alkalis are burnt together or better passed over activated charcoal when by their combination, hydrochloric acid is produced. $H_2 + Cl_2 = 2HCl$.

Properties

Physical—Hydrogen chloride is a *colourless gas* with a *pungent, suffocating* smell. It is heavier than air and can be liquefied to a colourless liquid.

Its critical temp. is 51·45°C and the critical pressure 81·5 atmos.

The gas *fumes in moist air* and is extremely soluble in water. It is highly *ionized* in aqueous solution, and is the *strongest acid known*. HCl is soluble in alcohol, acetic acid, etc.

Distillation of Hydrochloric acid.—When a strong solution of hydrogen chloride in water is distilled, the gas escapes and the solution get diluted. On the other hand, when dilute hydrochloric acid is distilled, water escapes and the solution gets concentrated. The temp. in each case gradually rises to 110°C at 760 mm., when no further change takes place, and the solution containing 20·24% of HCl by wt. distils over unchanged. This 20·24% sol. of HCl is called a *constant boiling solution or mixture* (*eutectic*).

Chemical.—It neither burns in air nor supports combustion It is strongly acidic and turns blue litmus red.

With ammonia it gives white fumes of ammonium chloride. Aqueous HCl acts upon many metals like Zn, Fe, Mg liberating hydrogen and forming their chlorides. Ag, Hg, Au are not acted upon by the acid ; while Cu, in presence of air and Pb dissolves in *hot* conc. HCl. It gives *aqua regia* with nitric acid and is oxidised by other oxidizing agents. It is decomposed into the elements by electricity. It gives white precipitates of the *respective chlorides* with soluble silver, mercurous and lead salts.

Test.—(1) Hydrochloric acid gas gives dense white fumes with ammonia.

(2) When it is heated with manganese dioxide, greenish yellow chlorine gas is evolved with a characteristic odour.

(3) When a solution of hydrochloric acid in water is added to silver nitrate solution, a curdy white ppt. of silver chloride insoluble in nitric acid, but soluble in ammonium hydroxide is obtained.

Use.—Hydrochloric acid is used in the laboratory as a reagent ; in the manufacture of chlorine ; in dyeing industry ; in the manufacture of colours, phosphates, and metallic chlorides ; in preparing *aqua regia* ; and a *very* dilute solution of HCl in water is used with HNO_3 in medicine.

Volumetric composition of hydrochloric acid gas and its molecular formula.

It can be shown by combining one volume of dry hydrogen and one volume of dry chlorine within an explosion tube that no change in volume takes place. In other words, *one* volume of hydrogen combines with *one* volume of chlorine to produce *two* volumes of hydrochloric acid gas.

The Formula HCl

1 vol. of hydrogen combines with 1 vol. of chlorine to give 2 vols. of hydrochloric acid gas.

Let n be the number of molecules present in one vol. of H.

$\therefore$ n molecules of hydrogen combine with n molecules of chlorine to give $2n$ molecules of hydrogen chloride (*Avogadro*).

Or, 1 molecule of hydrogen combines with 1 molecule of chlorine to give 2 molecules of hydrochloric acid gas.

Or, 2 atoms of hydrogen combine with 2 atoms of chlorine to give 2 molecules of hydrochloric acid gas (—for *H* and *Cl* molecules are *diatomic*).

Or, 1 atom of hydrogen combines with 1 atom of chlorine to give 1 molecule of hydrochloric acid gas.

Hence, the formula of Hydrochloric acid gas is HCl.

Confirmation of the formula HCl.—The density of hydrogen chloride is 18·25. ∴ its Mol. wt. is 2×18·25=36·5, which agrees with the formula HCl.

Chlorides.—Chlorine forms two distinctive types of binary compounds—(1) chlorides of metals and (2) chlorides of non-metals.

Chlorides of metals : They are really salts of hydrochloric acid.

Preparation :

(1) The chlorides of metals above hydrogen in the electrochemical series may be prepared by the direct action of hydrochloric acid (or HCl gas) on the metal.

$$Fe + 2HCl = FeCl_2 + H_2 \quad \| \quad Zn + 2HCl = ZnCl_2 + H_2$$

In the reducing atmosphere of hydrogen, the lower (*ous*) chloride is formed with metals which form two series of chlorides.

(2) The chlorides of metals may also be prepared by the action of hydrochloric acid on the oxides, hydroxides or the carbonates of metals.

$$MgO + 2HCl = MgCl_2 + H_2O \quad \| \quad ZnCO_3 + 2HCl = ZnCl_2 + CO_2 + H_2O$$

After the reaction is over, the solution is evaporated to crystallisation.

(3) Non-metallic chlorides and a few metallic chlorides in the anhydrous state are prepared by the direct action of chlorine on the element. $2Fe + 3Cl_2 = 2FeCl_3 \quad \| \quad 2P + 5Cl_2 = 2PCl_5$.

Chlorine being a powerful oxidising agent, generally the highest (*ic*) chloride is produced.

(4) Some industrially important chlorides in the anhydrous state may be prepared by the action of chlorine on a mixture of the oxide of the metal and carbon.

$$Al_2O_3 + 3C + 3Cl_2 = 2AlCl_3 + 3CO.$$

(5) Insoluble chlorides of metals are prepared by double decomposition.

$$AgNO_3 + HCl = AgCl + HNO_3$$
$$Pb(NO_3)_2 + 2NaCl = PbCl_2 + 2NaNO_3$$

Properties.—Chlorides of metals differ widely from those of non-metals in their properties.

Chlorides of metals are generally crystalline solids soluble in water with the exception of AgCl, $PbCl_2$ (soluble in hot water), Hg_2Cl_2 and Cu_2Cl_2 which are insoluble.

Chlorides of non-metals are usually liquids which are hydrolysed completely by water. $PCl_3 + 3H_2O = H_3PO_3 + 3HCl$

Some metallic chlorides *e.g.*, chlorides of iron, aluminium, tin etc., are partially hydrolysed by water.

$$FeCl_3 + 3H_2O = Fe(OH)_3 + 3HCl.$$

When heated, some chlorides decompose yielding the metal or a lower chloride.

$$2AuCl_3 = 2Au + 3Cl_2 \quad \| \quad 2CuCl_2 = Cu_2Cl_2 + Cl_2$$

Some hydrated chlorides of metals decompose on heating liberating hydrochloric acid gas.

$$MgCl_2, 6H_2O = Mg(OH)Cl + HCl + 5H_2O$$

Hypochlorous acid and hypochlorites

Hypochlorous acid may be prepared by passing a stream of chlorine through water, containing precipitated mercuric oxide or, calcium carbonate in suspension.

$$HgO + H_2O + 2Cl_2 = 2HOCl + HgCl_2$$

$$CaCO_3 + H_2O + 2Cl_2 = CaCl_2 + CO_2 + 2HOCl$$

Properties.—Hypochlorous acid is known in dilute solution only. Concentrated solution decomposes giving oxygen. Hence it is a powerful oxidising and bleaching agent.

Hypochlorites.—These are salts of hypochlorous acid. Potassium, sodium and calcium hypochlorites may be prepared by the action of chlorine on cold solutions of the hydroxides of the respective metals. Sodium hypochlorite, NaOCl may be prepared by the electrolysis of a cold solution of sodium chloride without any diaphragm so that chlorine liberated at the anode may come in free contact with the alkali produced at the cathode.

$$2NaOH + Cl_2 = NaCl + NaOCl + H_2O$$

Sodium chloride is also produced at the same time.

Hypochlorites are more stable than hypochlorous acid and find extensive use as bleaching agents.

Bleaching powder, $Ca(OCl)Cl$.

Bleaching powder is prepared by passing chlorine over dry slaked lime. (i) The slaked lime is spread on the floor of a chamber provided with wooden stirrers. Dry chlorine *freed from HCl* and CO_2, is passed in. (ii) The gas is absorbed by lime which is raked from time to time. (iii) The temp. is not allowed to rise above 40°C and the mass is left as such for about 24 hours. (iv) At the end of the period, powdered slaked lime is dusted inside the chamber to get rid of the excess of chlorine. Bleaching powder is now taken out.

$$Ca(OH)_2 + Cl_2 = Ca(OCl)Cl + H_2O.$$

Properties—It is a *white amorphous* powder which smells strongly of chlorine. It gradually loses its chlorine when left exposed to the air. Treated with water, bleaching powder decomposes into calcium chloride and calcium hypochlorite.

$$2Ca(OCl)Cl + [H_2O] = CaCl_2 + Ca(OCl)_2 + [H_2O].$$

With *very* dil. HCl, we get HOCl ; while with ordinary dilute acids, we get Chlorine.

$$\begin{aligned} Ca(OCl)Cl + HCl &= CaCl_2 + HOCl. \\ Ca(OCl)Cl + 2HCl &= CaCl_2 + H_2O + Cl_2. \\ Ca(OCl)Cl + H_2SO_4 &= CaSO_4 + H_2O + Cl_2. \end{aligned}$$

Use.—It is used for bleaching purposes, and as a disinfectant.

Bleaching.—The articles (yarn or cloth) to be bleached is first boiled with dil. caustic soda solution to make it free from grease, etc, and is then washed with water. The washed article is now steeped in a cold, dilute solution of bleaching powder in water. It is then taken out and treated with dil. HCl or dil. H_2SO_4, when the article is bleached by the evolved chlorine. The *bleached article* is removed, washed with water, then with 5% Na_2CO_3 sol. and is dipped into a bath of an *antichlor* (sodium bisulphite or sodium thiosulphate solution). It is finally taken out, thoroughly washed with water and dried.

Available Chlorine means the amount of chlorine expelled by the action of dilute acids on one gm.-mol. wt. of dry bleaching powder.

Chlorates :—Chlorates are salts of chloric acid, $HClO_3$. Chloric acid is unknown in pure form, but a dilute solution may be prepared by the action of sulphuric acid on barium chlorate.

$$Ba(ClO_3)_2 + H_2SO_4 = BaSO_4 + 2HClO_3$$

Chlorates are obtained by passing Cl_2 into hot solutions of an alkali. Thus potassium chlorate is obtained by the action of chlorine on hot caustic potash solution.

$$6KOH + 3Cl_2 = 5KCl + KClO_3 + 3H_2O$$

On cooling, the sparingly soluble potassium chlorate crystallises out.

Properties: The chlorates are all soluble in water, the least soluble being potassium chlorate. Chlorates are stable at ordinary temperatures, but when heated, decompose into chlorides and oxygen.

$$2KClO_3=2KCl+3O_2$$

They are powerful oxidising agents. When a chlorate such as pot. chlorate is mixed with organic matter, charcoal, sulphur or realgar (arsenic sulphide) etc., and the mixture is struck by a hammer or heated, it explodes.

Uses.—Potassium chlorate is used in the laboratory for the preparation of oxygen. It is used in the manufacture of matches and fire works. It is also used for treatment of throat infections in the form of lozenges.

Bromine

Symbol, Br. At. wt., 80. At, no., 35. Vapour density, 80.

History.—Bromine was discovered by Balard.

Occurrence.—It does not occur free in nature. In combination it occurs—as *bromides of sodium, potassium, magnesium* and *calcium*; in sea-water; in mineral water; and in salt deposits, especially at Stassfurt. It also occurs as *silver bromide, AgBr.*

(1) Laboratory Method of Preparation.—Heat a mixture of potassium bromide, manganese dioxide and conc. sulphuric acid in a stoppered glass retort the end of which is introduced into a small flask kept cold by means of a stream of water (fig. 54). Bromine is liberated, which distils over and collects inside the flask.

$$2KBr+3H_2SO_4+MnO_2=2KHSO_4+MnSO_4+2H_2O+Br_2.$$

(2) Bromine can also be prepared by passing chlorine into a strong solution of a bromide. $2KBr+Cl_2=2KCl+Br_2$.

Manufacture of bromine

(1) Formerly bromine was obtained almost exclusively from carnallite of Stassfurt deposit which contains a little $MgBr_2$ as an impurity. Carnallite is first dissolved in water and concentrated, when potassium chloride crystallises out and is removed. The hot mother liquor containing magnesium chloride and magnesium bromide is treated with chlorine in a tower which sets free bromine. Bromine is vaporised by steam which is blown in from the bottom of the tower.

Bromine escapes by an outlet at the top and is condensed in a spiral condenser (fig. 73).

$$MgBr_2 + Cl_2 = MgCl_2 + Br_2$$

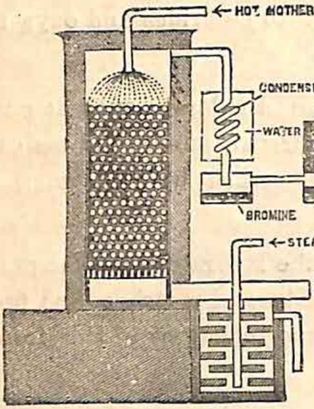


Fig. 73—Manufacture of bromine.

(2) **From Sea water**—Sea water contains small amount of sodium bromide, which is now the chief source of bromine. Sea water contains about 70 parts of bromine per million parts of water in the form of bromide. A cubic mile of sea water weighing 4 billion tons can furnish 300,000 tons of bromine. Sea water is made slightly acidic with sulphuric acid and then allowed to trickle down a tower containing a stream of chlorine rising upward. Bromine is set free from the bromides by chlorine which is then blown out of water by a current of air and absorbed in a concentrated sodium carbonate solution. A mixture of sodium bromide and sodium bromate is thus obtained. $3Na_2CO_3 + 3Br_2 = NaBrO_3 + 5NaBr + 3CO_2$

When required, bromine is set free by means of sulphuric acid.

$$NaBrO_3 + 5NaBr + 3H_2SO_4 = 3Na_2SO_4 + 3Br_2 + 3H_2O$$

Properties

Physical.—At the ordinary temperature bromine is a heavy mobile, dark-red *liquid* possessing a very irritating odour. It is the only liquid non-metallic element at the ordinary temp. Bromine is poisonous. Its action on the mucous membranes is worse than that of chlorine. It attacks skin producing corrosive sores. Bromine has a specific gravity of 3·188 at 1°C and it boils at 59°C. In the *vaporous state* its molecule is *diatomic*. At the ordinary temperature bromine rapidly evaporates, if exposed in an open vessel and the vapours given off attack the eyes. It dissolves alcohol, ether, chloroform, carbon disulphide and acetic acid giving *reddish-brown* solution.

Add chlorine water to a solution of KBr. The solution is coloured red owing to the liberation of bromine. Now shake the liquid with a little carbon disulphide (or chloroform). Bromine dissolves in carbon disulphide (or in chloroform) producing a reddish brown solution.

$$2KBr + Cl_2 = 2KCl + Br_2$$

$$Br_2 + CS_2 \rightarrow \text{Reddish brown solution.}$$

Like chlorine, bromine dissolves in water giving *bromine-water*, which possesses the colour and smell of bromine. Like chlorine-water, *bromine-water* also gives bromine hydrate (Br_2, $8H_2O$) at 0°C.

Chemical.—Bromine is non-inflammable and *ordinarily* a *non-supporter* of combustion. Br_2 and H_2 do not combine at the ordinary temp. But a jet of burning hydrogen continues to burn in bromine-vapour. It combines directly with most of the metals, and with phosphorus and arsenic, giving the corresponding bromides. It is a mild *oxidising agent* and exhibits *feeble bleaching properties*. It oxidises sulphites into sulphates. $Na_2SO_3+Br_2+H_2O=Na_2SO_4+2HBr$; and H_2S into HBr and sulphur. $H_2S+Br_2=2HBr+S$. Like *chlorine-water*, bromine-water decomposes *on exposure to light*, giving off oxygen. $2H_2O+2Br_2=4HBr+O_2$. With cold caustic soda or caustic potash solution, bromine gives the hypobromite and the bromide.

$$Br_2+2KOH=KBr+KOBr+H_2O$$

while with the hot sol. of the alkalis it gives the bromate and bromide.

$$3Br_2+6KOH=KBrO_3+5KBr+3H_2O$$

Bromine, therefore, resembles chlorine in its chemical properties, *but it is less active than chlorine.* Bromine readily attacks organic substances such as starch, skin, etc. turning them yellow. It *does not directly* combine with carbon and nitrogen. It liberates iodine from an iodide. $2KI+Br_2=2KBr+I_2$

Test.—*Bromine* can be recognized by its deep-red colour and irritating odour. (2) It turns *Starch paste orange-yellow*. (3) When shaken with CS_2 or ether, bromine dissolves in the liquid giving a *reddish-brown solution.*

N. B.—Br_2-vapour and N_2O_4 are *nearly* of the same colour. They are distinguished from each other thus:—(i) N_2O_4 does not dissolve in CS_2: but (ii) it dissolves in water giving a *colourless* sol. containing HNO_3 and HNO_2.

Use.—Bromine is necessary for preparation of bromides used in medicine and in photography. It is used as a disinfectant, as an oxidising agent, in organic synthesis, and in dye industry.

Bromine in very large quantities finds application in petroleum industry.

Hydrobromic acid (*Hydrogen bromide*)

Formula, HBr Mol. wt., 81 Density, 40·5

(1) Hydrobromic acid may be prepared synthetically by passing a mixture of hydrogen and bromine through a heated tube containing finely divided platitum or platinised asbestos. $H_2+Br_2=2HBr$.

(2) Hydrobromic acid may be prepared by the action of phosphoric acid on potassium bromide.

$$KBr+H_3PO_4=KH_2PO_4+HBr$$

N.B. Conc. Sulphuric acid cannot be used, for it oxidises HBr into Br_2 and SO_2
$KBr+H_2SO_4=KHSO_4+HBr \parallel 2HBr+H_2SO_4=2H_2O+SO_2+Br_2$

(3) Laboratory Preparation—It is prepared by dropping bromine from a dropping funnel to a mixture of red phosphorus and water kept in a flask.

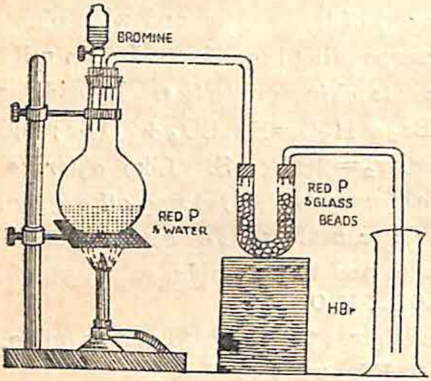


Fig. 74—Prep. of hydrobromic acid.

Bromine combines with phosphorus to produce tri-and pentabromides of phosphorus which are decomposed by water to produce hydrobromic acid. (Fig. 74).

$$2P+3Br_2=2PBr_3$$
$$2P+5Br_2=2PBr_5$$
$$PBr_3+3H_2O=3HBr+H_3PO_3$$
$$PBr_5+4H_2O=5HBr+H_3PO_4$$

Any unchanged bromine is reconverted into HBr by passing it through a U-tube loosely packed with moist red phosphorus. The gas is collected by the upward displacement of air.

If aqueous hydrobromic acid is desired, the gas is passed into water by means of an antisuction device as adopted in the case of aqueous hydrochloric acid (see prep. of HCl, fig. 72).

A solution of HBr can be obtained conveniently by passing H_2S or SO_2 into bromine water and distilling the liquid.

$H_2S+Br_2=2HBr+S \parallel SO_2+Br_2+2H_2O=2HBr+H_2SO_4$

Properties

Physical.—Hydrogen bromide is a *heavy, colourless gas.* It fumes in moist air and possesses pungent smell. It can be easily liquefied. It is highly soluble in water.

Chemical.—Hydrogen bromide is neither combustible nor a supporter of combustion. It is slightly decomposed at 800°C and is readily attacked by chlorine. Thus when chlorine is passed into a solution of hydrobromic acid in water, free bromine is liberated and HCl is formed. $2HBr+Cl_2=2HCl+Br_2$. Potassium immediately liberates hydrogen from HBr and forms potassium bromide.

$$2HBr+2K=2KBr+H_2.$$

It is an acid, turns blue litmus red and forms salts which are called bromides. Thus hydrobromic acid very closely resembles hydrochloric acid in properties, but hydrogen bromide is less energetic. Pure aqueous HBr is a colourless liquid. It dissolves Fe, Zn, Cu, Ag, Pb, etc. Aqueous HBr is decomposed by oxygen in sunlight and turns yellow from liberation of bromine ; $4HBr + O_2 = 2H_2O + 2Br_2$. A mixture of HNO_3 and aqueous HBr acts like *aqua regia*.

Test for HBr and Bromides

(1) Add silver nitrate solution to hydrobromic acid or a *soluble* bromide ; a *yellow-white* ppt. of silver bromide, insoluble in conc. HNO_3 and soluble with difficulty in ammonia, is obtained (*Cf*. chlorides).

$$KBr + AgNO_3 = KNO_3 + AgBr \parallel HBr + AgNO_3 = HNO_3 + AgBr.$$

(2) Add chlorine water to a solution of HBr or a bromide in water and shake the solution with carbon disulphide. CS_2 is coloured brown.

(3) Add conc. H_2SO_4 to HBr or a bromide, when *red vapours* of bromine are given off (*more copiously* when the mixture is heated with MnO_2).

Bromides are binary compounds of bromine with another element either a metal or a non-metal. The bromides resemble corresponding chlorides in their modes of preparation and properties. Metallic and non-metallic bromides may be prepared by the direct action of bromine on the element.

$$Zn + Br_2 = ZnBr_2 \parallel 2P + 5Br_2 = 2PBr_5$$

Metallic bromides may be obtained by the action of aqueous hydrobromic acid on metals like zinc, iron etc. which dissolve with evolution of hydrogen. Bromides are also obtained by neutralising aqueous hydrobromic acid with oxides, hydroxides and carbonates of metals. Bromides are more soluble than corresponding chlorides. Bromides of silver, lead and mercurous mercury are, however, insoluble in water. Sodium and potassium bromides are used in medicine and silver bromide in photography.

Hypobromites—When bromine acts on cold dilute caustic soda solution, sodium hypobromite is obtained.

$$2NaOH + Br_2 = NaBr + NaOBr + H_2O$$

Hypobromites are unstable and are rapidly converted into a mixture of bromate and bromide.

$$3NaOBr = NaBrO_3 + 2NaBr$$

Hypobromites like hypochlorites are used as oxidising and bleaching agents.

Bromates.—The bromates are very similar to chlorates and are obtained in the same way. Like chlorates, bromates are oxidising agents.

Iodine

Formula, I_2 At. wt., 127. At. no. 53.

History.—Courtois, a manufacturer of saltpetre near Paris, discovered iodine.

Occurrence.—Iodine is not found free in nature. It occurs in combination with some metals. Sea-water, sea-weeds, sponges, sea-animals, etc, contain small quantities of iodine compounds.

Iodine is present in cod-liver oil, in the thyroid glands of animals and in many springs. Chili saltpetre (Caliche) also contains iodine in the form of sodium iodate, and brine from petroleum wells contains iodine as iodides.

Preparation. (1) **Laboratory method**—Take a mixture of potassium iodide, MnO_2 and conc. H_2SO_4 in a stoppered glass retort the end of which is introduced into a small flask kept cold by means of a stream of water (fig. 54). Heat the flask, when iodine is evolved which *sublimes off* and condenses inside the flask in the form of black shining scales.

$$2KI+3H_2SO_4+MnO_2=2KHSO_4+2H_2O+I_2+MnSO_4.$$

(2) Iodine can also be obtained from potassium iodide by treating KI solution with chlorine or bromine. $2KI+Cl_2=2KCl+I_2$

Manufacture

1. **From Sea-weeds.**—Deep sea-weeds collect iodine compounds from sea water. The ash known as *kelp* obtained by burning the dried weeds contains iodide of sodium and potassium along with other compounds of these metals. The impurities such as sulphates, chlorides etc. are removed by crystallisation. The mother liquor contains iodides of sodium and potassium which is heated with manganese dioxide and concentrated sulphuric acid in iron stills having lead still-heads. Iodine sublimes off and is condensed in a series of earthenware receivers called *aludels*. (fig. 75).

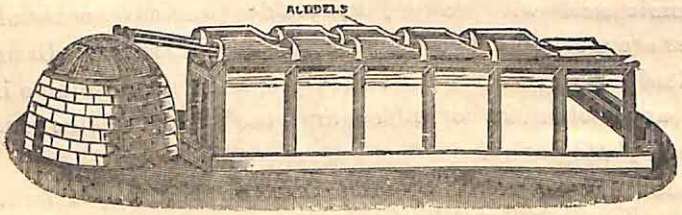


Fig. 75—Industrial prep. of Iodine from kelp.

$$2NaI+3H_2SO_4+MnO_2$$
$$=2NaHSO_4+MnSO_4+I_2+2H_2O.$$

2. **From Crude Chili Saltpetre (Caliche)**—Caliche contains about 0·2% of iodine in the form of sodium iodate which is separated

from the bulk of less soluble sodium nitrate by crystallisation. The mother liquor is now treated with sodium bisulphite when iodine separates out in the solid form. Crude iodine obtained is purified by resublimation.

$$2NaIO_3+5NaHSO_3=3NaHSO_4+2Na_2SO_4+I_2+H_2O$$

In America, most of the iodine is now-a-days obtained from petroleum brine.

Properties : Physical.—Iodine is a *blackish-grey* crystalline *solid* of metallic lustre. It is usually obtained in the form of scales. Its specific gravity is 4·94, and it melts at 114·2°C. It vaporises *very slowly* at the ordinary temp. When heated, it gives off violet (or purple-coloured) vapours, which smell like dilute chlorine. In the *vaporous* state iodine molecule is *diatomic* but at very high temps. it becomes monatomic. Iodine molecules dissociate with rise of temperature. $I_2 \rightleftarrows I+I$. It is very slightly soluble in water, much more soluble in a solution of potassium iodide in water. It is fairly soluble in many organic solvents ; alcohol, ether, acetone, chloroform, benzene, carbon disulphide, etc. The colour of the solutions differs with different solvents,—carbon disulphide, chloroform, etc, give *violet* solution ; while water, KI-solution, ether, etc. give *brown* solution.

Iodine also turns starch solution blue.

Add chlorine water to a solution of KI in water. The solution turns brown due to the liberation of Iodine. $2KI+Cl_2=2KCl+I_2$

Divide the resultant solution into two parts : (1) To one part, add a little CS_2 and shake and then allow the mixture to settle. The CS_2 layer at the bottom will be found to have a violet colour.

(2) To the other part, add a freshly prepared solution of starch. An intense blue colouration is produced. The blue colour disappears on heating, but reappears on cooling.

Chemical.—Iodine-vapour is neither combustible nor ordinarily a supporter of combustion. Hydrogen and iodine combine directly when heated in presence of spongy Pt. White phosphorus first melts and then bursts into flame whem brought into contact with iodine. It also combines with mercury, iron filings, zinc, K, etc. Iodine resembles chlorine and bromine in its chemical properties, but it is rather *less energetic*. It possesses practically no bleaching properties. Iodine dissolves in conc. HNO_3 giving iodic acid. $I_2+10HNO_3=2HIO_3+4H_2O+5N_2O_4$. It also dissolves in *cold* and *dilute* KOH or NaOH sol. giving the iodide and the hypoiodite, the latter being hydrolysed into hypoiodous acid. With hot NaOH or KOH sol. iodine gives the iodides and the iodates.

$$2KOH + I_2 = KI + KOI + H_2O$$
$$KOI + H_2O = KOH + HOI$$
$$6KOH + 3I_2 = KIO_3 + 5KI + 3H_2O$$

Iodine reacts with $KClO_3$ giving KIO_3 and free chlorine.

$$2KClO_3 + I_2 = 2KIO_3 + Cl_2$$

Iodine reacts with sodium thiosulphate to give sodium tetrathionate and sodium iodide. $2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI$

Test.—Iodine is recognised by (1) the violet colour of its vapours; it (2) turns starch solution blue, (3) dissolves in CS_2 forming a violet solution and (4) produces iodoform when warmed with alcohol (or acetone) and dilute alkali.

Use.—Iodine is used in medicine; in the manufactnre of dyes, iodoform, KI, NaI, etc, ; and in chemical analysis.

Hydriodic Acid (*Hydrogen iodide*)

Mol. formula, HI. Mol. wt. 128 Vapour density, 64

Preparation.—(1) *Synthesis*,—Hydrogen iodide may be prepared by passing a mixture of hydrogen and iodine-vapour over heated spongy Pt which acts as a catalytic agent. $H_2 + I_2 = 2HI$.

(2) **Laboratory Method of Preparation.**—Pour water slowly from a dropping funnel, fitted to a flask containing a mixture of *red* phosphorus and iodine. HI is evolved. Cool the flask by dipping in water. Allow the gas to pass through a U-tube containing moist red phosphorous and glass beads (fig. 74). Any iodine vapour coming out with HI is absorbed by *moist* red P in the U-tube, and HI passes on. Collect hydrogen iodide by the upward displacement of air. The gas is dried by *anhydrous* CaI_2 or P_2O_5 and *may* be collected over mercury *very carefully*. $2P + 3I_2 = 2PI_3 \parallel 2PI_3 + 6H_2O = 2H_3PO_3 + 6HI$.

Aqueous HI.—(1) It is obtained by dissolving the gas in water. Connect the end of the delivery tube of the above apparatus (fig. 74) with the stem of a funnel dipping just below the surface of water in a beaker (fig. 72). HI, generated in the flask, dissolves in water in the beaker, and aqueous HI is obtained.

(2) A solution of HI in water can be conveniently prepared by passing H_2S or SO_2 through water containing iodine in suspension. The liquid is then distilled. The distillate is aqueous HI.

$H_2S + I_2 = 2HI + S \parallel SO_2 + I_2 + 2H_2O = H_2SO_4 + 2HI$.

Properties

Physical.—Hydriodic acid is a very heavy colourless gas at the ordinary temp and, like HBr and HCl, it is highly soluble in water.

The gas can be easily condensed to a liquid under a pressure of four atmospheres, and at 0°C.

Chemical.—Hydrogen iodide does not burn nor does it support combustion. It is unstable. It slowly decomposes (*dissociates*) into its elements when exposed to sunlight and breaks up much more quickly when heated. Thus if a heated wire be thrust into the gas, the violet vapour of iodine at once makes its appearance. Aqueous solution is strongly *acidic* and turns *blue* litmus red. Solution of hydrogen iodide in water, when freshly prepared, is *colourless*, but it gradually turns brown in sunlight and *air*, owing to separation of free iodine, $4HI + O_2 = 2H_2O + 2I_2$. On account of this instability, and the consequent tendency to produce nascent hydrogen, hydriodic acid acts as a *powerful reducing agent*. It reduces sulphuric acid ; hence, as already stated, the gas cannot be prepared by the action of sulphuric acid on an iodide. It also reduces Cl_2, Br_2, and HNO_3 and other *oxygenated* compounds. Both the gas and the solution in water are decomposed by Cl_2 and Br_2 with the liberation of iodine.

$$H_2SO_4 + 2HI = I_2 + SO_2 + 2H_2O$$

$$2HNO_3 + 2HI = I_2 + 2NO_2 + 2H_2O$$

$$Br_2 + 2HI = I_2 + 2HBr \quad \| \quad Cl_2 + 2HI = I_2 + 2HCl.$$

Iodides.—Iodides are binary compounds of iodine with metals or non-metals. Metallic iodides are salts of hydriodic acid and can be obtained by the action of hydriodic acid on a metal, or its oxide, hydroxide or carbonate. Some of the iodides may be prepared by the direct action of iodine on the elements.

$$2P + 5I_2 = 2PI_5$$

$$Hg + I_2 = HgI_2$$

Tests for HI and Iodides :

(1) Add conc. H_2SO_4 to HI or an iodide. Iodine is liberated.

(2) Add $AgNO_3$ solution to a solution of HI or of an iodide in water. A yellow ppt. of AgI insoluble in NH_4OH and also in HNO_3 is obtained.

(3) Shake a solution of HI or an iodide in water with CS_2 and Cl_2-water. CS_2 is turned violet.

Hypoiodite and iodates.—They are very similar to corresponding hypochlorites and chlorates and are obtained by analogous reactions.

$$\underset{\text{Pot. hypoiodite}}{2KOH + I_2 = KI + KOI + H_2O}$$

$$6KOH + 3I_2 = 5KI + KIO_3 + 3H_2O$$

N. B. Pot. hypoiodite undergoes hydrolysis to form hypo-iodous acid. $KOI + H_2O = KOH + HOI.$

hypoiodous acid.

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Comparison of the Halogens

(1) **Resemblance.**—(1) None of them occur in nature in the *free state.* (2) They are all monovalent. (3) They all possess bad odour. (4) They all unite with Hydrogen giving rise to acids. (These Hydrogen compounds are all colourless gases which fume strongly in moist air. They are extremely soluble in water and are strongly acidic in character). (5) They all combine directly with the metals. (6) They may all be prepared by a similar process. (7) They all directly combine with Phosphorus giving Phosphorus halides.

(2) **Gradation in change of Properties with the increase of At. wts.**

	F	Cl	Br	I
(1) *At. wt.*	19	35 5	80	127
(2) *State of aggregation.*	Gas	Gas	Liquid	Solid
(3) *Colour of vapour.*	*Pale* greenish yellow	Greenish yellow	Brownish-red	Violet
(4) *Odour*	*Peculiar irritating* smell.	*Pungent and irritating* smell	Smell like that of Chlorine but *more irritating to nose and throat*	Smell like that of chlorine and *intensely irritating to the eye and nose.*
(5) *Solubility* In *water.*	decomposes *water.*	Fairly soluble	Fairly soluble	Very slightly soluble
(6) *Heaviness* or *Sp. gr.*	Slightly heavier than air.	2½ times heavier than air.	Sp. gr. 3'188 at 0°C.	Sp. gr., 4'9.
(7) *Reaction with Hydrogen.*	Unites *readily with* H_2 even in the dark with *explosion.*	Unites *readily with* H_2 in *sunlight* with *explosion.*	Unites with H_2 *less energetically* than F or Cl and only when *heated.*	Unites with H_2 *least energetically,* but more so when *heated* in presence of a *catalytic agent.*
	HF is *stable.*	HCl is *less stable* than HF.	HBr is decomposed by heat.	HI is decomposed by *slight heat.*
(8) *Bleaching action.*	Decomposes Organic bodies.	Readily bleaches vegetable colouring matter.	Bleaches more slowly than Chlorine.	*Possesses practically no bleaching* properties.
(9) *Chemical activity.*	*Most* active. Liberates Cl, Br, I from Chlorides, Bromides and Iodides respectively	*Less* active than Fluorine ; displaces Br and I from Bromides and Iodides respectively.	*Less* active than Chlorine ; displaces Iodine from Iodides.	*Least* active, cannot displace F, Cl or Br from Fluorides, Chlorides or Bromides.
(10) *Action on starch sol.*	Attacks water of the starch sol.	No change in colour of starch sol.	Starch sol. is coloured *orange yellow.*	Starch sol. is coloured *blue.*
(11) *Action on Alkalis* (i) *Cold sol.* (ii) *Hot sol.*	Attacks water of the sol. also gives Fluorides and F_2O	(i) Chloride & Hypochlorite. (ii) Chlorate and Chloride.	(i) Bromide & Hypobromite. (ii) Bromate & Bromide.	(i) Iodide & Hypoiodite, then HOI (ii) Iodate and Iodide

Exercise

1. Describe the expts. you have made in the laboratory to demonstrate the principal properties of chlorine. *Mad. 1911, C. U., 1907,' Pat., 1930*

2. Chlorine is said to be *very active*. Describe expts. where the activity is shown in a marked degree, and where there is lack of activity.

3. How would you prepare chlorine without the application of heat or electricity? *Nag., 1935 ; C. U., 1926.*

4. How is HCl manufactured? Give its uses and its action on Zn, S, HgO, MnO_2, Fe_2O_3, Mg, NaOH, KNO_3. *C. U., 1919, '21, '31*

5. How is bromine prepared on a large scale? Describe its action on (i) Potassium iodide (ii) sulphuretted hydrogen and (iii) sulphurous acid.

6. Describe Moissan's method of preparation of fluorine. Show that fluorine, chlorine, bromine and iodine are justifiably grouped together. *C. U., 1921, '43, '44, '56 ; Cam. Jun. ; Punj., 1942 ; Bom, B. A.*

7. What experiments would you make to show the difference in properties between a mixture of equal vols. of hydrogen and chlorine and the compound formed by the chemical union of these two gases? How would you obtain bromine from HBr? Give equations.

8. How is iodine obtained from kelp? Describe its important physical and chemical properties. Can you prepare HBr and HI in the same way in which HCl is prepared? If not, why? How do you get a solution of HI in water? *Punj., 1919 '30 ; All., 1932 ; C, U, 1941, '21, '26, '28, '34, '42, '47 ;*

9. Explain with equations what happens when :
   (*a*) Chlorine gas is passed into hot and conc. solution of potassium hydroxide.
   (*b*) Chlorine gas is passed into an aqueous solution of H_2S.
Cal. Pre U. 1961.

10. Describe the laboratory method of preparation of chlorine. State its important properties and uses. Explain with equation what happens when chlorine gas is passed into hot and conc. solution of sodium hydroxide. *Cal. Pre-U. 1962.*

11. How would you prepare concentrated solution of Hydrochloric acid? Give a neat sketch of the apparatus you will use. Describe with equations the action of hydrochloric acid on (*a*) Manganese dioxide (*b*) Calciam carbonate and (*c*) Silver nitrate solution. *Cal. Pre-U. 1963.*

12. Describe how would you prepare bleaching powder. Give outlines of the metals with equations. Describe also the uses of the compound. *Cal. Pre-U. 1964.*

13. Describe how you would prepare hydrochloric acid gas in the laboratory. Give a neat sketch of the apparatus. State with equation what happens when chlorine is passed into a solution of KBr. *Cal. Pre-U. 1965.*

14. Describe briefly the preparation of Iodine from Potassium Iodide. *Cal. Pre-U. 1965.*

15. Describe briefly under what conditions and with what results HCl and MnO_2 react together. *Cal. Pre-U., 1966.*

16. How is pure and dry chlorine gas prepared in the laboratory? Give a neat sketch of the apparatus.

What happens when chlorine gas is passed into :
   (*a*) cold and dil. aqueous solution of NaOH,
   (*b*) aqueous solution of sulphur dioxide.
and (*c*) aqueous solution of potassium iodide.

Give equations. *Cal. Pre-U., 1967.*

17. Describe briefly the preparation, properties and uses of Bleaching Powder. *Cal. Pre-U. 1967.*

18. What happens when—
   (a) Chlorine gas is passed through hot conc. solution of NaOH solution.
   (b) An excess of conc. solution of Ammonia is added to chlorine. Describe with equation. *Cal. Pre-U. 1970*

CHAPTER XVIII

PHOSPHORUS AND ITS COMPOUNDS

Phosphorus

Mol. formula, P_4 At. wt., 31.   At. no., 15.   Vapour-density, 62,

History.—Phosphorus was first discovered by the alchemist Brand who obtained it by distilling a mixture of sand with concentrated urine, probably with the addition of charcoal. It is called phosphorus (*phos*=light ; *phero*=I carry), for it glows in the dark.

Occurrence.—Phosphorus is not found in nature in the *free* state. In combination, it is very widely distributed as phosphates like—

Phosphorite, $Ca_3(PO_4)_2$

Chlor-apatite, $3Ca_3(PO_4)_2, CaCl_2$

Fluor-apatite, $3Ca_3(PO_4)_2, CaF_2$

Vivianite. $Fe_3(PO_4)_2, 8H_2O$.

Phosphorus is present in soil as calcium phosphate, from where it is taken up by plants. So phosphorus is present in cereals like wheat. From the plants, it passes into the animal kingdom. Hence it is present in egg yolks, nerves, brains and bones. When bones are freed from fat and carbonaceous matters (blood, bits of flesh etc.) by burning them off, the residue is bone ash (80%. cal. phosphate). Bone ash is an important source of phosphorus.

Manufacture of Phosphorus

The Modern Electrical Process (Readman, Parker, Robinson's process)—A mixture of calcium phosphate (either *bone ash* or *phosphate rocks*), sand and coke is fed through the hopper, by a warm conveyer (fig. 76) into a closed electric furnace and is heated to high temperature by means of *electric current.*

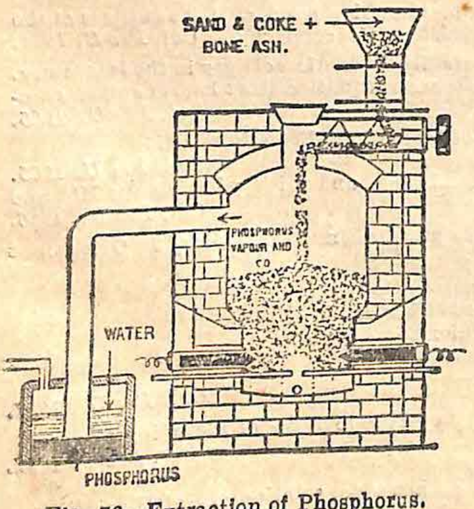

Fig. 76—Extraction of Phosphorus.

The furnace is made of brick-work. There is an outlet *near the top* for the escape of hot gases and vapours of phosphorus, and another at the bottom for taking out the slag. Electric current is passed through two stout carbon rods fixed near the bottom of the furnace so as to form an '*arc*' inside the mixture which is thus very strongly heated.

Reactions.—At the high temp. (1200°—1500°C) produced inside the furnace,—(i) calcium-phosphate reacts with silica producing calcium silicate and P_2O_5. (ii) Phosphorus pentoxide is then reduced by carbon and phosphorus is set free. (iii) Calcium silicate melts and sinks to the bottom, whence it is run off. (iv) Phosphorus vapours and CO escape through the outlet near the top, and are passed into water, where phosphorus vapours condense. Fresh mixture is introduced and the process is thus made continuous.

$$Ca_3(PO_4)_2 + 3SiO_2 = 3CaSiO_3 + P_2O_5.$$
$$2P_2O_5 + 10C = 10CO + 4P.$$

Purification of Phosphorus.—Crude phosphorus contains carbon and other impurities. It is purified by melting it under water and then filtering it through canvas or chamois leather. It is now cast into sticks. A *purer* product may be obtained by redistillation.

Properties

Physical.—Ordinary (also known *white* and, not very *correctly* called, *yellow* and *non-metallic*) phosphorus is a translucent, almost colourless wax-like solid. It is soft and can be cut with a knife. Its sp. gr. is 1·8. It melts at 44°C and boils at 287°C. The liquid and vapour are colourless ; and the vapour-density shows that the molecule of the vapour is P_4. It partially *dissociates* at high temperatures giving P_2 molecules. $P_4 = P_2 + P_2$.

It is practically insoluble in water, but it readily dissolves in carbon disulphide, chloroform, benzene, etc.

Chemical.—When left exposed to moist air, phosphorus undergoes spontaneous oxidation producing white fumes. During this oxidation it *phosphoresces*, or *glows*, especially in the dark, emitting a greenish white light (*cold flame*).

The *glowing* of phosphorus is *probably* due to the presence of O_3 formed during its oxidation. It catches fire, in *moist* air, at about 30°C. Hence it is always kept under water. Phosphorus is chemically very active. It readily combines with the halogens, metals and sulphur at the ordinary temperature. When burnt in air, the main product is P_2O_5. It *reduces* H_2SO_4, HNO_3, $CuSO_4$, etc. It reacts with NaOH and KOH solutions giving off phosphine, PH_3.

$$4P + 3NaOH + 3H_2O = PH_3 + \underset{\text{sod. hypophosphite.}}{3NaH_2PO_2}$$

Phosphorus is very poisonous, the vapours causing diseases of jaw bones.

Allotropic modifications of Phosphorus.—Phosphorus exists in different allotropic modifications of which the most *important* are :—

(1) **White Phosphorus** and (2) **Red Phosphorus.**

Red Phosphorus

It is formed when white phosphorus is heated to 250°C in an inert gas in presence of a trace of iodine.

Manufacture of Red Phosphorus.—White phosphorus is heated to 240°C—250°C, out of contact with air, in a covered cast iron vessel provided with a safety tube. The temperature is not allowed to rise above 250°C. The solid, left in the vessel after heating, is first ground to powder with water, and then boiled with caustic soda solution to remove any unchanged white phosphorus likely to be present. It is finally washed with water and dried.

Properties

Red phosphorus is a chocolate (*violet-red*) solid, having a specific gravity of 2·2. It does not glow in the dark and has no taste or smell. It melts at 500°C—600°C when heated under pressure. It is *insoluble* in carbon disulphide and in water. Red phosphorus is less chemically active than ordinary phosphorus and is not poisonous. Heated in air, it ignites at about 240°C with the production of phosphorus pentoxide. It combines with the halogens and sulphur but less energetically than the white variety. When red phosphorus is strongly heated, it is vaporised. The vapours condense into white phosphorus. It is not attacked by KOH or NaOH solution and it is a feeble conductor of electricity.

Red and Ordinary (*i.e.* White) Phosphorus compared		WATER WHITE P.
Property	*Red. P.*	*Ordinary (i.e., white) P.*
1. Colour	Chocolate *(violet-red)*	Almost Colourless
2. Smell, etc.	Odourless and tasteless.	Garlic smell.
3. Specific gravity	2·2.	1·8.
4. Melting-point	500°-600°C.	44°C.
5. Action of water	Insoluble.	Almost insoluble
6. Action of CS_2. Chloroform, etc.	Insoluble.	Readily soluble.
7. Exposed to air	No phosphorescence (no glow, no oxidation)	Phosphorescence (glow and oxidation).
8. Ignition temp.	240°C.	30°C.
9. Electric current	Feeble conductor	Very feeble conductor.
10. Hot NaOH sol.	No action	Readily reacts with *hot* NaOH sol. giving off PH_3.
11. Chlorine gas	Takes fire in Cl_2, if heated	Spontaneously burns in Cl_2
12. Physiological action	Not poisonous.	Highly poisonous.
13. Chemical activity	Less active than *white* P.	Very active
14. Stability	*Stable* at the *ord. temp.*	*Less stable at the ord temp.*

Uses of Phosphorus.—(1) *White* phosphorus is used in the manufacture of red Phosphorus, P_2O_5 and *lucifer* matches. (2) *Red* phosphorus is used in the preparation of HI and HBr in the laboratory; in the manufacture of *safety* matches; and for producing vacuum in electric lamps.

Phosphine (Phosphuretted Hydrogen)

Formula, PH_3. Mol. wt., 34. Density, 17.

(1) Laboratory Method of Preparation.—Phosphine is prepared in the laboratory by heating *white* phosphorus with a solution of caustic soda or caustic potash.

$$4P + 3KOH + 3H_2O = \underset{\text{Pot. hypophosphite}}{3KH_2PO_2} + PH_3$$

Take small pieces of *white* phosphorus with a fairly strong solution of caustic potash in a flask provided with a delivery tube and an inlet tube dipping in caustic potash solution (fig. 77). Pass a stream of coal gas through the inlet tube to remove the air from the flask. Now gently heat the flask. Phosphine (mixed with traces of P_2H_4) is evolved and as each bubble escapes into the air, it bursts into flame, forming *vortex rings* of white smoke of phosphorus pentoxide. Potassium hypophosphite is left in the solution.

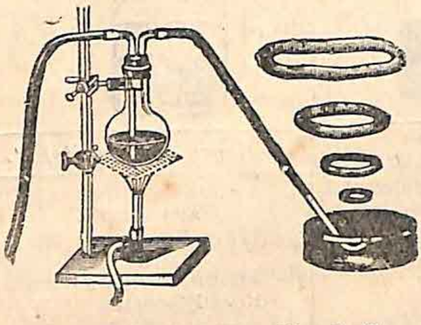

Fig. 77—Prep. of Phosphine in the Laboratory.

Collection.—The spontaneous inflammability of phosphine is due to the presence of P_2H_4 as an impurity. The gas, as such, may be collected over water ; but it is safer to make the gas free from P_2H_4 by passing it through a U-tube kept immersed in a freezing mixture in which P_2H_4 condenses, and then collect PH_3 over water.

Non-spontaneously inflammable phosphine is obtained by using an **alcoholic** solution instead of the aqueous solution, of caustic potash (for P_2H_4 dissolves in alcohol). $PH_4I + KOH = KI + H_2O + PH_3$.

Properties.—Phosphine is a colourless gas heavier than air, and possesses an offensive smell like that of rotten fish. It is not spontaneously inflammable, when pure. When heated, it is decomposed into its elements ; and when ignited in air or in oxygen, it burns forming phosphorus pentoxide. $2PH_3 + 4O_2 = P_2O_5 + 3H_2O$.

It is very slightly soluble in water, and is highly poisonous. It has no action upon litmus. PH_3 bears an analogy with NH_3 in having some *basic* properties. For example, it forms a series of *phosphonium* compounds—phosphonium chloride, phosphonium bromide and phosphonium iodide—like the corresponding *ammonium salts*.

$$PH_3 + HCl = PH_4Cl \parallel PH_3 + HBr = PH_4Br \parallel PH_3 + HI = PH_4I.$$

Phosphine is decomposed by chlorine or bromine. A jet of the gas spontaneously ignites, when introduced into chlorine gas or bromine vapour. $PH_3 + 3Cl_2 = 3HCl + PCl_3 \parallel PH_3 + 4Cl_2 = PCl_5 + 3HCl$. The pure gas is completely absorbed by bleaching powder. Phosphine possesses **reducing** properties. When passed into solution of $CuSO_4$, $HgCl_2$, etc., it precipitates the phosphides of the metals.

$$3CuSO_4 + 2PH_3 = 3H_2SO_4 + Cu_3P_2.$$

$$3HgCl_2 + 2PH_3 = 6HCl + Hg_3P_2.$$

Like ammonia it also combines with the chlorides of Al, Sn etc.

Test.—It may be detected—(1) by its bad smell of rotten fish ; (2) it gives a *black* ppt. of copper phosphide when passed into $CuSO_4$ solution ; and (3) a black ppt. of silver when passed into $AgNO_3$ solution.

Absorbents.—(i) Bleaching powder and (ii) Ag_2SO_4 solution.

Oxides and Oxy-acids of Phosphorus

Oxides	Oxy-acids
Phosphorus oxide, P_2O_3 or P_4O_6	Phosphorous acids, H_3PO_3
	Orthophosphoric acid, H_3PO_4
Phosphorus pentoxide, P_2O_5	Metaphosphoric acid, HPO_3

Phosphorus Oxide, P_2O_6

(Phosphorus trioxide, phosphorus anhydride)

Formation—This oxide is formed, with the pentoxide when phosphorus oxidises in air at the ordinary temperature.

Preparation—Take a few pieces of white phosphorus in a hard glass tube. Connect the tube with a condenser the end of which is attached to a U-tube kept immersed in a freezing mixture. There is a plug of *glass wool* in the middle of inner tube of the condenser. Gently heat phosphorus ; and draw a *slow* current of air by a pump. P_4O_6, mixed with a *little* P_2O_5, is formed which passes on and condenses in the inner tube of the condenser. Now replace *cold* water in the jacket by *warm* water at 50°—60°C when P_4O_6 volatilises and condenses in the U-tube, while, P_2O_5 vapours, if any, are arrested by the glass-wool (fig. 78).

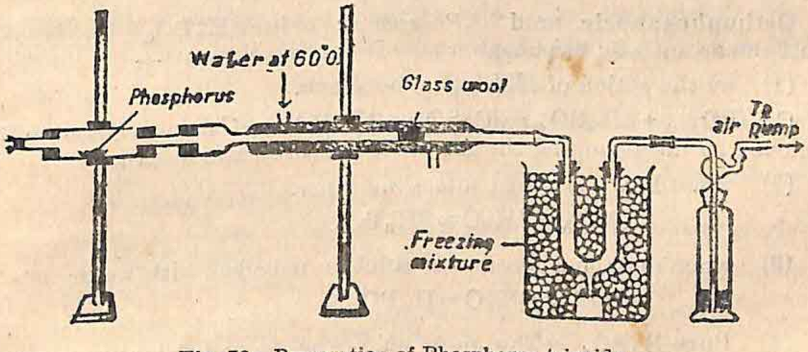

Fig. 78—Preparation of Phosphorus trioxide.

Properties—It is a wite, crystalline solid, waxy in appearance, having a garlic odour. It melts at 23·8°C. Its vapour density is 110, and therefore, the correct formula is P_4O_6. Phosphorus trioxide rapidly oxidises into the pentoxide in air or in oxygen. It burns in Cl_2 as also in warm oxygen. Cold water attacks it very slowly giving phosphorous acid. $P_4O_6 + 6H_2O = 4H_3PO_3$; while with hot water, a violent reaction takes place producing red phosphorus, phosphine, and phosphoric acid. It is poisonous.

Phosphorus pentoxide :—(*Phosphoric Anhydride*)P_2O_5.

Preparation.—This oxide is readily prepared by burning dry phosphorus in a current of *excess* of dry air, when the pentoxide condenses as a voluminous powder known as *flower of phosphorus.*

$$4P + 5O_2 = 2P_2O_5.$$

The oxide, thus obtained contains small quantities of the lower oxides which are converted into the pentoxide by passing the fumes, mixed with dry oxygen, over heated platinised asbestos.

Properties—Phosphorus pentoxide is a white, hygroscopic powder which readily absorbs moisture from the atmosphere. It is without smell, when pure, but has got a slight garlic odour due to the presence of other oxides as impurities. It sublimes when heated. Phosphorus pentoxide reacts with *cold water*, with a hissing sound resembling the quenching of red-hot iron, giving *metaphosphoric acid.* $P_2O_5 + H_2O = 2HPO_3$. When the solution is *boiled*, or when P_2O_5 is thrown into *hot* water, *orthophosphoric acid* is formed. $P_2O_5 + 3H_2O = 2H_3PO_4$. It can abstract the elements of water from HNO_3, H_2SO_4, alcohol, etc.

$$C_2H_5(OH) + P_2O_5 = C_2H_4 + 2HPO_3.$$

Use.—Phosphorus pentoxide is largely used—(i) as a desiccating or drying agent ; and (ii) for preparing phosphoric acid.

Orthophosphoric acid.—(*Phosphoric acid*)—H_3PO_4—It is the most important acid of phosphorus. It may be obtained—

(1) by the action of H_2SO_4 on bone-ash.

$Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4$. Calcium sulphate is removed by filtration and the filtrate is evaporated to a syrup.

(2) when P_2O_5 is added to *boiling water.*

$$P_2O_5 + 3H_2O = 2H_3PO_4.$$

(3) when metaphosphoric acid solution is boiled with water

$$HPO_3 + H_2O = H_3PO_4.$$

(4) **Pure H_3PO_4.**—The pure acid may be conveniently prepared by boiling phosphorus with nitric acid.

$$4P + 10HNO_3 + H_2O = 4H_3PO_4 + 5NO_2 + 5NO.$$

Experiment.—Boil *red* phosphorus with conc. HNO_3 diluted with an *equal volume* of water. After phosphorus has completely dissolved, evaporate the liquid in a platinum dish on a sand-bath, with a little more conc. nitric acid to oxidise any H_3PO_3, that may be formed, into H_3PO_4. Cool the residue left. Dissolve it in water, and again evaporate it at 110°C. Now *cool* the solution over conc. H_2SO_4 in a *vacuum desiccator*, surrounded by freezing mixture, when crystals of *pure* orthophosphoric acid are slowly deposited.

Properties.—Pure orthophosphoric acid is a *colourless*, *deliquescent*, crystalline solid, melting at 42°C. Ordinarily it is used in the form of a syrupy solution. It readily dissolves in water. When heated to 250°C, it gives *pyrophosphoric acid.* $2H_3PO_4 = H_4P_2O_7 + H_2O$: while at 316°C it is decomposed into *metaphosphoric acid*, which, on subsequent cooling, solidifies to a glass-like mass called *glacial phosphoric acid* having the composition according to some chemists, $(HPO_3)n$. $H_3PO_4 = HPO_3 + H_2O$.

When pyrophosphoric acid or metaphosphoric acid is boiled with water, it is transformed back into orthophosphoric acid.

Orthophosphates

Orthophosphoric acid is tribasic and forms three series of salts, called orthophosphates (or phosphates).

Preparation.—The metallic orthophosphates can be prepared by neutralising the acid with the oxides, hydroxides and carbonates of the metals ; or by double decomposition.

$$2NaOH + H_3PO_4 = 2H_2O + Na_2HPO_4$$

$$Na_3PO_4 + 3AgNO_3 = Ag_3PO_4 + 3NaNO_3$$

Properties—The normal phosphates of all metals, with the exceptions of those of Na, K and (NH_4), are insoluble in water. They are all soluble in mineral acids. The alkali phosphates, produced by the gradual replacement of hydrogen atoms in a molecule of H_3PO_4, have different reactions in solution. Thus—

NaH_2PO_4 (a *primary phosphate*, an acid salt, called mono-sodium dihydrogen phosphate) has *acid* reaction.

Na_2HPO_4 (a *secondary phosphate*, an acid salt, called di-sodium hydrogen phosphate) has *faintly alkaline*, practically *neutral* reaction.

Na_3PO_4 (a *tertiary phosphate*, a normal salt, called tri-sodium phosphate) has *alkaline* reaction.

Action of heat on phosphates—

(i) Primary phosphates, on being heated, give metaphosphates.
$NaH_2PO_4 = NaPO_3 + H_2O$.

(ii) Secondary phosphates, on being heated, give pyrophosphates.
$2Na_2HPO_4 = Na_4P_2O_7 + H_2O$.

(iii) Tertiary phosphates *do not* decompose on being heated.

N. B.—This is also the case with the potassium salts.

Phosphorus trichloride, PCl_3

Preparation—It is prepared by the direct action of chlorine on dry white phosphorus which is kept over sand in a retort from which air has been displaced by chlorine. The retort is gently heated on a water bath. Now chlorine is passed into the retort through a bent tube, the distance between which and the white phosphorus is so adjusted that no phosphorus distils or phosphorus pentachloride is formed. At the end of the experiment, the retort is heated to 72°-78°C when phosphorus trichloride.distils over. $2P+3Cl_2=2PCl_3$

Properties—Pure phosphorus trichloride is a colourless, liquid and may be preserved in sealed flasks. Its vapour-density is *normal.* It fumes strongly in moist air, due to the formation of HCl.

$$PCl_3+3H_2O=3HCl+H_3PO_3,$$

It gives a white compound $PCl_3, 6NH_3$, with ammonia.

Use.—It is used in organic preparations and in organic analysis.

Phosphorus Pentachloride PCl_5

Preparation.—Fit a wide-mouthed dry bottle with a stopper through which pass a dropping funnel and two bent tubes one of which is longer than the other. The shorter bent tube acts as an outlet. Cool the bottle in water containing ice (fig. 79). Now pass a stream of dry chlorine into the flask through the long bent tube and, at the same time, drop PCl_3 slowly from the funnel so that the gas is always *in excess*. Combination takes place immediately producing a quantitative yield of solid PCl_5.

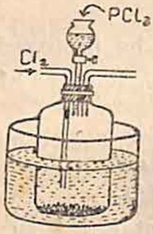

Fig. 79—Prep. of PCl_5

$$PCl_3+Cl_2=PCl_5.$$

Properties—Pure PCl_5 is almost a colourless solid which sublimes at 100°—160°C. When exposed to air, it gives off copious and irritating fumes. When heated, its vapours dissociate into PCl_3 and Cl_2. PCl_5 reacts with organic compounds containing hydroxyl group liberating hydrochloric acid, the hydroxyl group being replaced by a chlorine atom.

$$\underset{\text{Alcohol}}{C_2H_5OH}+PCl_5=C_2H_5Cl+HCl+POCl_3$$

Use.—In organic preparations and in organic analysis.

Exercise

1. Describe the allotropic modifications of phosphorus. How may red phosphorus be obtained from white phosphorus and *vice-versa* ? Give the uses of phosphorus. *Mad., 1925 ; Bom., 1939 ; C. U., 1943, '45, 47, 52,*

2. How are the oxides of phosphorus prepared ? What is the action of water on them ? *Mys., Trav., Andh. : Pat., 1927*

3. What is the most important sources of phosphorus ? How is the element prepared on a large scale ? Mention the chief properties and uses of phosphorus. *Bom, 1924 ; Mad., 1931 ; Nag., 1922, '33, C.U., 1931, '33, '43, '45 : All. 1933.*

4. How will you obtain—(*a*) phosphine (*b*) PCl_3 and (*c*) P_2O_5 from phosphorus? *C. U., 1933, '37.*

5. What takes place when phosphorus is heated (i) in dry air, and (ii) with HNO_3? What is the connection between the products obtained?

6. Describe briefly the preparation of phosphorus from bone ash. *Cal. Pre-U., 1965.*

7. Give outlines, with equations, of the preparation of yellow phosphorus starting from bone ash. Starting with yellow phosphorus, how could red phosphorus be prepared? How do the properties of red and yellow phosphorus differ? *Cal. Pre-U., 1967.*

CHAPTER XIX

SULPHUR AND ITS COMPOUNDS

Sulphur

Symbol, S At. wt., 32 At. No. 16

Sulphur is known from time immemorial. We find mention of it in the Bible. Its use was known in ancient India. The very name sulphur is probably derived from the Sanskrit *sulvery* meaning the enemy of copper.

Occurrence.—Sulphur occurs in nature both (1) in the free state and also (2) as compounds.

(1) In the free state sulphur is found extensively in volcanic regions in Sicily and in Texas and in Lousiana in America. In Sicily, sulphur occurs nearer the surface in a formation of gypsum, clay and sulphur (20%) but in Texas and Lousiana the deposit of sulphur occurs several hundred feet below the ground overlaid with beds of quicksand.

(2) In the form of compounds, sulphur occurs as (*a*) sulphide—Iron pyrites, FeS_2; galena, PbS; copper pyrites, $CuFeS_2$ etc; (*b*) as sulphates—gypsum, $CaSO_4, 2H_2O$, heavy spar, $BaSO_4$ etc, (c) Sulphur also occurs in volcanic gases and in the water of sulphurous springs in the form of sulphuretted hydrogen; (*d*) Sulphur is present also in the proteins of hair and eggs and in several other food stuffs such as onion, garlic, mustard oil etc, which generally leave a black stain on silver utensils.

In Sicily, sulphur is directly mined and purified from the associated impurities—sand, stone, gypsum, etc. by stacking it on the slope of a brick-built kiln (leaving air spaces) and setting fire to it, so that a part of the sulphur burns and the heat produced melts the remainder which runs away from the unmolten solid impurities. In Lousiana, the mining of sulphur became a problem. Direct mining was impossible as the mines evolved poisonous sulphuretted hydrogen fumes, which overpowered miners. The source, therefore remained unavailable for a long time after its discovery. Herman Frasch first solved the problem. He sank three concentric pipes into the bed of sulphur. Through the outermost one, superheated water sufficiently hot (180°C) to melt sulphur is sent down, Compressed air is pumped through the inner-most one. Molten sulphur is forced up in a strem through the middle one (fig. 80),

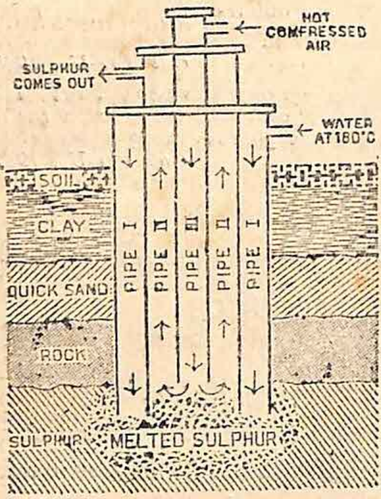

Fig. 80—Frasch Process

Refining of crude sulphur— After mining, sulphur is further refined by vaporising it in a closed chamber with an outlet leading to another where sulphur vapour first condenses on the cold walls as a light yellow powder consisting of minute crystals called *flowers of sulphur*. But later on, as the chambers get heated, sulphur melts and collects on the floor as an amber coloured liquid. This is run off and cast into cylindrical rods called *roll sulphur* (fig. 81).

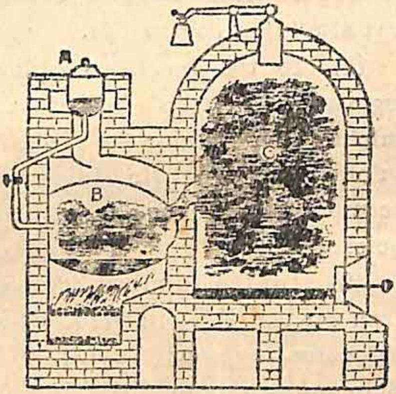

Fig. 81—Refining of crude sulphur.

Allotropic modifications of Sulphur : Their Preparation and Physical Properties—Sulphur assumes *four* **important** allotropic forms of which *two* are *crystalline* and *two amorphous*.

(A) **Crystalline forms :** (1) Rhombic or Octahedral Sulphur.
(2) Prismatic or Monoclinic Sulphur.

(B) **Amorphous or non crystalline forms :**
(3) Plastic Sulphur,
(4) Milk-of-Sulphur.

Colloidal Sulphur is another variety of sulphur.

(1) **Rhombic or Octahedral Sulphur**—as the name shows crystallises in rhombic or octahedral forms. The crystals have the forms of two four-sided pyramids joined by their bases (fig. 82). It is stable at temperatures below 96·5°C. It melts at 113°C and has a sp. gravity of 2·05. It is soluble in carbon disulphide. It is transparent and pale yellow in colour. Rhombic sulphur is prepared by dissolving roll sulphur in carbon disulphide and allowing the solution to evaporate slowly. Well defined crystals of rhombic sulphur are deposited from the solution.

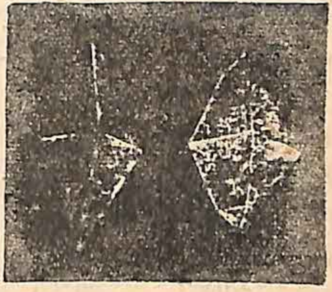

Fig. 82—Crystals of Rhombic sulphur.

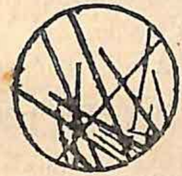

Fig. 83—Prismatic sulphur

(2) **Prismatic or Monoclinic Sulphur** is stable between 96·5°C and 118·6°C which is its melting point. It is transparent, waxy yellow in colour and has a sp. gravity of 1·93. It is soluble in carbon disulphide. Monoclinic crystals are needle-shaped (fig. 83). They are most readily obtained by allowing molten sulphur to cool slowly in a dish. When a crust is formed on cooling, a hole is pierced through it and the molten sulphur from inside is poured out. The inside of the dish would be found to be lined with needle-shaped crystals of monoclinic sulphur.

(3) **Plastic Sulphur** is elastic as the name shows just like India rubber. Here it differs from the crystalline varieties of sulphur which are brittle. It also differs from them in being insoluble in carbon disulphide. It is unstable and slowly passes into the stabler rhombic variety.

It is prepared by heating sulphur to about 400°C, when sulphur is converted into a dark brown mobile liquid. It is now poured in a thin stream into cold water in a beaker. The substance which solidifies is plastic sulphur. (fig. 84).

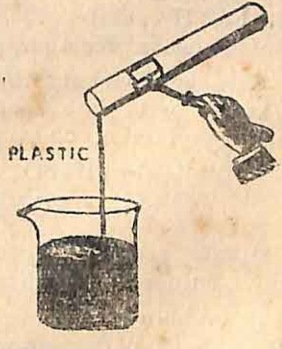

Fig. 84—Plastic sulphur

(4) **Milk of sulphur** is white in colour, soluble in carbon disulphide and is obtained by adding an acid to a poly-sulphide, *e.g.*, yellow ammonium sulphide.

$$(NH_4)_2S_2 + 2HCl = 2NH_4Cl + H_2S + S.$$

Colloidal sulphur—It is obtained when H_2S is passed into a cooled saturated solution of SO_2 in water. Colloidal sulphur is soluble in CS_2 and is used in medicine.

Properties

Physical.—Ordinary sulphur is a *pale-yellow*, *brittle*, *crystalline* solid. It appears *opaque*, although *pure* rhombic sulphur is *transparent*. Sulphur is insoluble in water but dissolves in carbon disulphide, benzene, and turpentine. It is a non-conductor of heat and electricity.

Action of heat on sulphur.—When heated, sulphur at first melts to yellow, mobile liquid at 113°C ; on raising the temperature furthur the colour darkens, the liquid loses its mobility, becomes viscous, and at 230°C it becomes almost solid and nearly black. Above 230°C it again becomes mobile and at 444°C it boils and gives off brownish-red vapour.

Sulphur (113°)→melts(160°)→	Mobile(230°)→	Black(300°)→	Mobile(444°)→boils.
	liquid pale yellow	viscid mass almost solid	liquid

Chemical.—Finely divided sulphur when exposed to the air and moisture is slowly oxidised with the formation of traces of sulphuric acid. It burns in air or in oxygen with a pale-blue flame forming sulphur dioxide. Sulphur combines directly with many metals (Cu, Ag, Fe, Hg, etc). when heated, to produce the sulphides. Iron and sulphur, heated together, produce iron sulphide. $Fe + S = FeS$

Sulphur does not dissolve in acids which are not oxidising agents. It reacts with hot conc. H_2SO_4 giving off SO_2. Conc. HNO_3 (especially fuming) oxidises sulphur to sulphuric acid.

$$S + 2H_2SO_4 = 3SO_2 + 2H_2O$$

$$S + 6HNO_3 = 6NO_2 + H_2SO_4 + 2H_2O.$$

Alkalis react with sulphur forming reddish-yellow solutions containing sulphides and thiosulphates.

It combines with carbon at a red heat forming carbon disulphide, and also with other non-metals like hydrogen, chlorine, etc.

$$2S + Cl_2 = S_2Cl_2.$$

Use.—*Crude sulphur* is a used in making sulphur dioxide which is required in the manufacture of sulphites, sulphuric acid, and for bleaching purposes. It is also used for making gun-powder, matches, vulcanite, etc. Sulphur is sometimes used as a disinfectant, and as a germ-killer. *Colloidal sulphur* is used in medicine, and *flowers of sulphur* as an insecticide.

Sulphur is required for the processing of rubber. Natural rubber has the disadvantage that it becomes soft and sticky when heated and is hence not suitable for the manufacture of rubber goods, particularly, automobile tyres. But if some sulphur is incorporated into natural rubber by heating, it becomes tougher and does not soften on heating. The process is known as *vulcanisation.*

Sulphuretted Hydrogen

(*Hydrogen sulphide* or *Hydrosulphuric acid.*)

Formula, H_2S. Mol. wt., 34. Density, 17.

Occurrence.—Sulphuretted hydrogen occurs in solution in certain mineral waters and also in volcanic gases. It is formed during the putrefaction of vegetable and animal matters which contain sulphur ; hence the familiar odour of rotten eggs.

Prepartion.—(1) **Synthetical.**—Sulphuretted hydrogen may be prepared synthetically by passing a mixture of hydrogen and sulphur vapour through a red-hot tube packed with pumic stone ; or by passing hydrogen into boiling sulphur. $H_2 + S = H_2S$.

(2) **Laboratory Method.**—In the laboratory, sulphuretted hydrogen is most conveniently prepared by the action of the cold, dil. hydrochloric or sulphuric acid upon ferrous sulphide. For *small quantities*, a Woulfe's bottle is used.

Experiment.—Place a few pieces of ferrous sulphide in Woulfe's bottle fitted with a thistle funnel and a delivery tube. Pour *dilute* H_2SO_4 down the funnel so that the end of the thistle funnel dips below the surface of the liquid (fig. 85). Reaction at once sets in and sulphure-

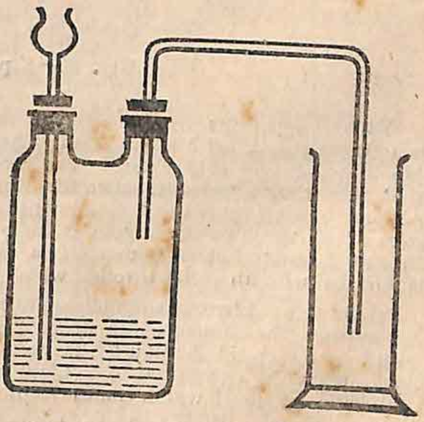

Fig. 85—Laboratory prep. of H_2S

tted hydrogen is evolved. Collect the gas by the upward displacement of air. It can also be collected over *warm* water

$$FeS + H_2SO_4 = FeSO_4 + H_2S.$$

Note that nitric acid cannot be used for preparing H_2S from a sulphide, for H_2S produced is *oxidised* by HNO_3 into sulphur, etc.

Comparatively *large quantities* of sulphuretted hydrogen are required intermittently in the laboratory for analysis. Hence it is always kept ready in all laboratories in the **Kipp's Apparatus** (fig. 86).

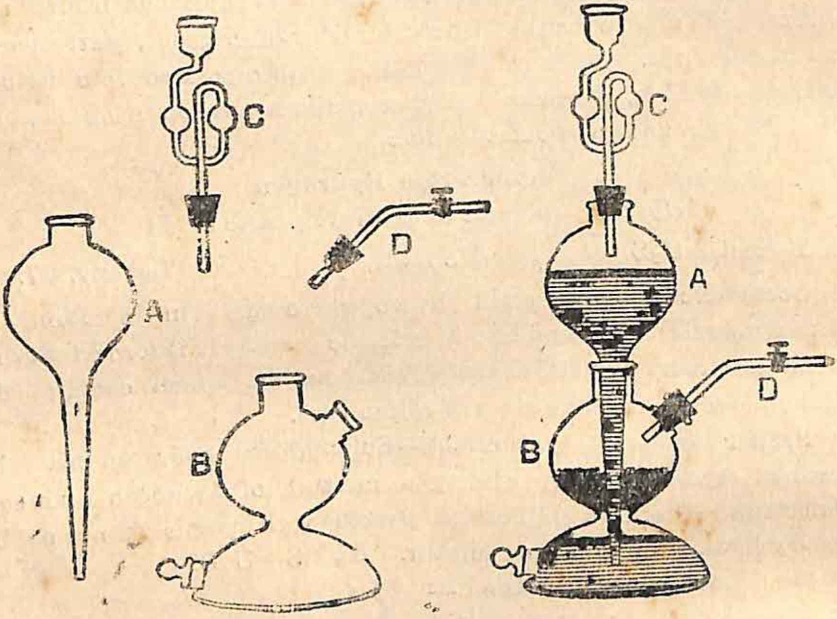

Fig. 86—Kipp's Apparatus

Kipp's Apparatus.—It consists of two detachable parts. The upper vessel is a glass globe (A) with a long stem. The lower portion consists of two glass globes joined together by a short neck. The lowermost globe is flattened at the bottom so that the whole apparatus, when fitted, may rest on it. The upper vessel serves the purpose of a big funnel and fits airtight into the neck of the central globe (B), the stem nearly touching the bottom of the lowermost globe. A glass stop-cock is attached to the central globe by means of a rubber stopper ; while the lowermost globe is provided with an outlet through which the waste liquid can be drawn off.

Small lumps of ferrous sulphide are introduced into the central globe of the Kipp's Apparatus. The stop cock is opened and dilute H_2SO_4 is poured down the safety funnel at the top till the liquid fills the lowest globe and then rises into the central globe. Here the acid comes in contact with the ferrous sulphide. Sulphuretted hydrogen is produced which comes out of the stop-cock.

When H_2S is not required, the stop-cock is closed ; H_2S collects in the central globe and its pressure forces H_2SO_4 out of this globe, H_2SO_4 rises up the stem and goes to the topmost globe. Thus, further action ceases. When H_2S is again required, the stop-cock is opened. H_2S escapes, and the pressure inside the central globe falls. H_2SO_4 again enters the globe, reacts with the lumps of ferrous sulphide and a fresh quantity of H_2S is evolved.

Drying Hydrogen Sulphide.—Sulphuretted hydrogen *cannot* be dried by conc. H_2SO_4, for the acid is *reduced* by the gas with the deposit of sulphur. $H_2S + H_2SO_4 = SO_2 + 2H_2O + S$.

For ordinary purpose, it may be dried by means of fused $CaCl_2$. It is best dried by *purified* P_2O_5.

Properties

Physical.—It is a *colourless gas* which smells like *rotten eggs*. It dissolves in cold water and imparts its own smell to the solution. The gas can be expelled from the solution by boiling. It is heavier than air. It can be liquefied comparatively easily.

Chemical.—Sulphuretted hydrogen burns with a blue flame when ignited producing sulphur or sulphur dioxide depending upon the amount of air present.

$2H_2S + 3O_2 = 2H_2O + 2SO_2$ (*excess of air or oxygen*)

$2H_2S + O_2 = 2H_2O + 2S$ (*limited supply of air or oxygen*)

$2H_2S + 2O_2 = 2H_2O + SO_2 + S$ (*ordinarily*).

It is not supporter of combustion. It is highly poisonous.

(*a*) *Reactions of Sulphuretted hydrogen as a reducing agent.*

Sulphuretted hydrogen is easily oxidised producing either sulphur or sulphur dioxide according to the nature of the oxidising agent. Hence it behaves as a reducing agent. For example, it reduces sulphuric acid to sulphur dioxide as has been mentioned already and nitric acid to nitric oxide, itself being mainly oxidised in each case to free sulphur.

$$H_2S + H_2SO_4 = 2H_2O + SO_2 + S$$

$$3H_2S + 2HNO_3 = 4H_2O + 3S + 2NO$$

Ferric chloride is reduced to ferrous chloride by sulphuretted hydrogen. Yellow ferric chloride solution turns light green (almost colourless) and the solution becomes cloudy due to separation of Sulphur. $2FeCl_3 + H_2S = 2FeCl_2 + 2HCl + S$

It also reduces sulphur dioxide to sulphur and halogens to their hydracids. $SO_2 + 2H_2S = 2H_2O + 3S \parallel Cl_2 + H_2S = 2HCl + S$.

(*b*) *Reactions of sulphuretted hydrogen as an acid.*

Sulphuretted hydrogen acts as a weak dibasic acid. It turns blue litmus red and reacts with bases to form salt and water.

$$NaOH + H_2S = NaHS + H_2O \parallel 2NaOH + H_2S = Na_2S + 2H_2O$$

The gas attacks metals like silver, lead, tin etc. producing a stain.

$$Sn\ (\text{Heated}) + H_2S = SnS + H_2$$

(c) *Precipitation of metallic sulphides.*

When sulphuretted hydrogen is passed through a solution containing metallic ion, the sulphide of the metal if insoluble, is precipitated.

$$CuSO_4 + H_2S = \underset{\text{Black}}{\downarrow CuS} + H_2SO_4$$

Sulphides of most metals are insoluble in water, exception being those of alkali and alkaline earth metals. Some metallic sulphides can be precipitated in acid solution, others in neutral or alkaline solution only. By controlling the acidity or the alkalinity (pH) of the solution, it is possible to precipitate certain metal ions and keep others in solution.

Sulphides of different metals have generally distinctive colours which may lead to their indentification. For example, zinc sulphide is white : antimony sulphide, orange : arsenic sulphide, yellow and mercuric sulphide, black. When sulphides of two or more metals have almost the same colour, they may be still differentiated by their behaviour towards different reagents. Thus copper sulphide may be distinguished from mercuric sulphide (both black) by the fact that copper sulphide dissolves in dilute nitric acid in which mercuric sulphide is insoluble.

Use of H_2S as a Chemical Reagent :

Sulphuretted hydrogen is hence used in qualitative analysis for (1) identifying metals, (2) separating one metal from another and (3) classifying metals into groups (see above).

Absorbents—(1) lead nitrate solution. (2) caustic potash or caustic soda solution.

Test—(1) It has a peculiar smell of rotten eggs.
(2) It turns lead acetate paper black.
(3) It produces a black stain on silver coins.

Sulphur Dioxide (*Sulphurous Anhydride*)

Formula, SO_2, Mol. wt., 64. Density, 32.

Occurrence.—Sulphur dioxide present in volcanic gases, in the springs of volcanic districts, and in the air of towns, where it is produced when coal containing sulphur compounds are burnt.

Laboratory Method of Preparation.—Take some copper turnings inside a flask, clamped to a retort stand, and fitted with a thistle funnel till the end of the funnel remains dipped under the surface of the acid. Now heat the flask on a piece of wire-gauge, and as soon as sulphur dioxide begins to be evolved, remove the source of heat. Collect the gas by the upward displacement of air. (fig. 87).

$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2.$$

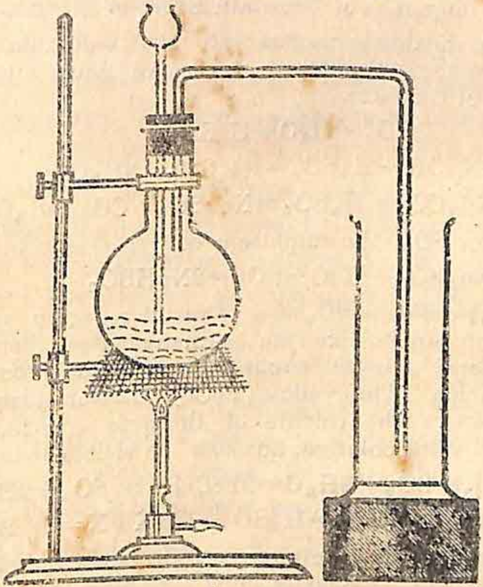

Fig. 87—Laboratory prep. of SO_2

To get *dry* and *fairly pure* SO_2, pass it through a wash-bottle containing conc. sulphuric acid and collect it over mercury.

Sulphur dioxide may also be prepared in the laboratory by the action of an acid on a sulphite or a bisuphite.

$$NaHSO_3 + HCl = NaCl + H_2O + SO_2.$$

Manufacture.—On a large scale sulphur dioxide is prepared

(i) by burning crude sulphur in air. $S + O_2 = SO_2$; or

(ii) by roasting iron pyrites in air. $4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2$.

Properties

Physical.—Sulphur dioxide is a *colourless gas*, having the peculiar *suffocating odour* of burning sulphur. It is poisonous. It is much heavier than air. It is highly soluble in water. It can be easily liquefied. Liquid SO_2 causes on evaporation intense cold, the temp. coming down to $-50^{\circ}C$.

Chemical.—The gas neither burns nor ordinarily supports combustion. It combines with oxygen in presence of catalysts like Pt, anhydrous $MgSO_4$, V_2O_5, etc.

(1) *Acid reaction*—The solution of SO_2 in water turns blue litmus sol. red and probably contains the *unstable* sulphurous acid.

$$SO_2 + H_2O = H_2SO_3.$$

The high solubility of SO_2 in water and also its acid reaction can be demonstrated by means of Fountain Experiment. (See Ammonia).

When sulphur dioxide is passed into the hydroxide or carbonate of a metal, we get the sulphite of the metal with the evolution of CO_2 in the case of the latter.

$$SO_2 + H_2O = H_2SO_3.$$

$$2NaOH + H_2SO_3 = Na_2SO_3 + 2H_2O$$

$$Na_2CO_3 + H_2SO_3 = Na_2SO_3 + CO_2 + H_2O$$

With excess of SO_2, the sulphite is converted into bisulphite.

$$Na_2SO_3 + H_2O + SO_2 = 2NaHSO_3$$

(2) *Reducing action.*—SO_2 is a powerful *reducing* agent and can reduce many substances like the permanganates, dichromates, etc. It also reduces *ferric* salts to *ferrous* salts ; chlorine, bromine and iodine into their hydracids. The yellow $FeCl_3$ solution turns light green (almost colourless). The colours of Bromine and Iodine solutions are discharged. With chlorine, however, no visible change occurs.

$$2FeCl_3 + SO_2 + 2H_2O = 2FeCl_2 + H_2SO_4 + 2HCl.$$

$$SO_2 + X_2 + 2H_2O = H_2SO_4 + 2HX \text{ (} X = Cl, Br \text{ or } I \text{)}$$

(3) *Bleaching action.*—Sulphur dioxide bleaches vegetable colour in presence of moisture. Put some red flowers after moistening them with water in a jar of sulphur dioxide. The red colour gradually fades and turns white. Like chlorine, it can not bleach in absence of moisture. Unlike chlorine which bleaches by oxidation, sulphur dioxide bleaches by reduction. Bleaching by sulphur dioxide is often temporary, the colour tending to come back. Bleaching by chlorine on the other hand is permanent.

(4) *Oxidising action*—Sometimes, sulphur dioxide can act as an oxidising agent. Thus heated particles of tin and iron burn when dropped into a jar of sulphur dioxide. Sulphur dioxide also oxidises sulphuretted hydrogen setting free sulphur.

$$SO_2 + 2H_2S = 3S + 2H_2O.$$

(5) Sulphur dioxide decomposes into sulphur when passed over heated carbon at 1200°C. $C + SO_2 = CO_2 + S$. This reaction proves the presence of sulphur in sulphur dioxide and is utilised in recovering sulphur from waste chimney gases.

Test—

(1) Sulphur dioxide can be recognised by its smell of burning sulphur and the bleaching action on vegetable colour.

(2) A drop of pot. permanganate solution held at the tip of a glass rod is decolorised when exposed to the gas.

(3) A blotting paper moistened with pot. dichromate is turned green by sulphur dioxide.

Absorbent—(*a*) alkalis and (b) pot. permanganate solution.

Use.—SO_2 is used as a disinfectant. Hospitals and rooms used by patients are sometimes fumigated, after the patients have vacated them, with sulphur dioxide. It is used in the manufacture of sulphuric acid and sulphites ; as a bleaching agent ; for preserving wine, meat, etc. ; in sugar manufacture ; and as a germ-killer. It is also used as an '*antichlor*' for removing the excess of chlorine from substances which have been bleached by chlorine. Liquid SO_2 is used as a refrigerating agent.

Sulphur trioxide, SO_3—Sulphur trioxide is only important in relation to sulphuric acid of which it is the anhydride. It can be prepared by distilling from a retort a mixture of conc. sulphuric acid and phosphorus pentoxide. $H_2SO_4 + P_2O_5 = SO_3 + 2HPO_3$.

It is obtained (as an intermediate product in the manufacture of sulphuric acid) by passing a mixture of sulphur dioxide and excess of oxygen over platinised asbestos heated to 450°C. $2SO_2 + O_2 = 2SO_3$.

Sulphur trioxide is a white silky crystalline solid. It reacts vigorously with water to produce sulphuric acid. $SO_3 + H_2O = H_2SO_4$.

Sulphuric Acid

Formula. H_2SO_4 Mol. wt., 98.

Sulphuric acid was known to the alchemists who obtained it first by distillation of green vitriol, $FeSO_4, 7H_2O$.

It is the most important of all acids and finds use in almost all chemical industries. The industrial progress of a country is measured by its annual consumption of sulphuric acid. Hence, it is rightly called the king of chemicals. There are two methods for its manufacture :

(A) Contact Process and (B) Lead Chamber Process

The basic reactions in both the processes are essentially the same.

(1) Burning sulphur or sulphide to produce sulphur dioxide.

$$S + O_2 = SO_2$$

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2$$

(2) Oxidising the sulphur dioxide with more air to sulphur trioxide. $2SO_2 + O_2 = 2SO_3$.

(3) Absorbing sulphur trioxide in water to produce sulphuric acid. $SO_3 + H_2O = H_2SO_4$.

(A) Contact Process :

Principle : The Contact Process, as we have seen from the foregoing discussion, is based on the ability of SO_2 to combine with Oxygen in presence of a catalyst like Pt to yield SO_3 and the reaction of the latter with water to produce H_2SO_4.

Condition of the Experiment :

(1) Air must be mixed with SO_2 in excess.

(2) The mixture of air and SO_2 must be absolutely free from dust and other impurities (particularly if the source of SO_2 is a sulphide) to avoid poisoning the catalyst.

(3) Temperature in the catalyst chamber (contact furnace) should be moderate (450°C). The reaction is exothermic and reversible. Hence, excessive rise of temp. causes decomposition of SO_3 produced. $2SO_2 + O_2 \rightleftharpoons 2SO_3 + 45{\cdot}2$ Cals.

(4) As the forward reaction is accompanied by diminution in volume, the yield of SO_3 should increase with increase of pressure according to a well-known principle of Physical Chemistry (Le Chatelier principle). The yield of SO_3 under atmospheric pressure is sufficiently high obviating the necessity of higher pressure.

(5) Catalysts, like Pt or V_2O_5 are used to hasten the process.

Details : Sulphur dioxide is produced by burning sulphur or pyrites in excess of air in ovens known as *pyrites burners.* The mixture of SO_2 and air is then thoroughly purified from dust particles and other impurities by leading it successively through a series of apparatuses

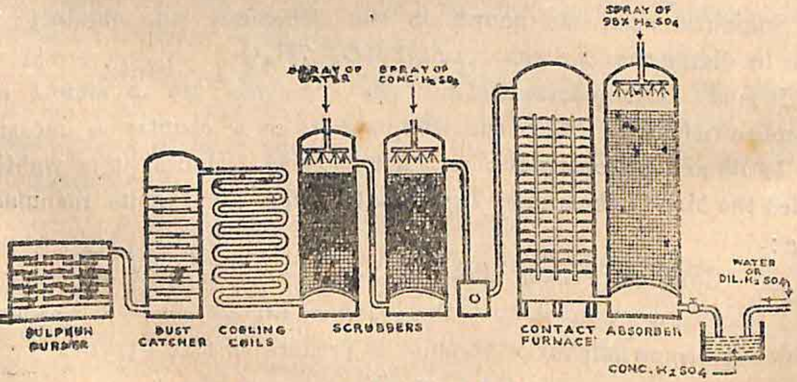

Fig. 88—Manufacture of Sulphuric acid—Contact process

such as Dust catchers[1] and towers packed with coke from the top of which water and conc. H_2SO_4 sprinkled down. The gas mixture is finally examined in a Tyndal box[2]. If found free from dust and other suspended particles, the SO_2-air mixture is allowed to enter the contact chamber after it has been preheated by the gases discharged from the latter. The contact furnace contains iron pipes packed with platinised asbestos (catalyst).

In the contact chamber in presence of the catalyst, sulphur dioxide is oxidised into sulphur trioxide. $2SO_2 + O_2 \rightleftarrows 2SO_3$.

The temperature is maintained around 450°C by the heat evolved during the process.

Sulphur trioxide is absorbed in a tower in 98% sulphuric acid producing oleum. (Sulphur trioxide is not absorbed readily in water).

A stream of dilute sulphuric acid or water is now mixed with oleum to make sulphuric acid of any desired strength.

$$SO_3 + H_2SO_4 = \underset{\text{oleum}}{H_2SO_4, SO_3}$$

$$H_2SO_4, SO_3 + H_2SO_4, H_2O = 3H_2SO_4.$$

(B) Lead Chamber Process :

Preparation of sulphuric acid in the laboratory to illustrate the principle of the Lead Chamber Process.

(i) *Theory*—When sulphur dioxide and oxygen (or air) are mixed with nitrogen dioxide in presence of steam or water, a series of reactions take place at the end of which sulphuric acid is obtained.

NO_2 parts with a portion of its oxygen which oxidises SO_2 into SO_3. SO_3 reacts with H_2O to produce H_2SO_4, while NO_2 itself is reduced into nitric oxide.

$NO_2 + SO_2 = SO_3 + NO$ ‖ $SO_3 + H_2O = H_2SO_4$.

Nitric oxide, thus formed, again combines with oxygen of the air producing NO_2. Thus NO_2 oxidises a further quantity of SO_2 into SO_3, which, in presence of water, is converted into more H_2SO_4.

$$2NO + O_2 = 2NO_2.$$

Thus there is no loss of nitric oxide, and the reactions go on in a cycle. And, theoretically at least, a small amount of the oxide of nitrogen can convert a relatively large quantity of SO_2 into sulphuric acid. Nitric oxide acts here as a '*carrier*', for it carries oxygen from the air to sulphur dioxide.

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[1] In modern plants, dust particles are usually removed by electrostatic methods by leading the gas mixture through an electrostatic separator.

[2] A Tyndal box is an apparatus in which suspended dust and other particles are rendered visible when viewed in a beam of light which is focussed on them in a direction at right angle to the direction of view.

(ii) *Substances required* :—

(*a*) Sulphur dioxide.	(*b*) Nitric oxide.
(*c*) Air.	(*d*) Steam or water.

(iii) *Details.*—Take a large flask fitted with a rubber stopper through which pass five glass tubes, four of these reach near the bottom of the flask, while the fifth is a short one and acts as an exit tube (fig. 89). Introduce air through the first tube into the flask, and then pass NO through the 2nd tube—by connecting it with a Woulfe's bottle in which the gas is generated by the action of HNO_3 of *moderate strength* on copper—till deep-red fumes are formed. Generate SO_2 in another flask by the action of hot conc. H_2SO_4 on copper and now pass the gas through the 3rd tube, when the red fumes, at first formed, disappear. Through the 4th tube pass excess of steam from a flask containing boiling water. Sulphuric acid is produced which collects as an oily liquid in the flask. The gases escape through the exit tube. Add a drop or two of the oily liquid to water. Test a portion of the sol. with *blue* litmus paper ; it turns *red*. Now add barium chloride sol. to the other portion ; a white ppt., insoluble in conc. HCl, is obtained. This proves the oily liquid to be sulphuric acid.

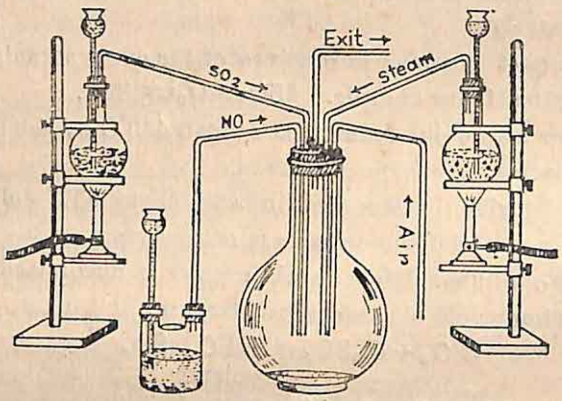


Fig. 89—Lab. prep. of sulphuric acid.

The Chamber Crystals—When the supply of steam is insufficient, instead of sulphuric acid, crystals having the composition $SO_2(OH)NO_2$ are found to be deposited on the walls of the flask (or on the walls of the Lead Chambers.) They are called **Chamber Crystals**, and they are decomposed by excess of steam.

$$2SO_2(OH)NO_2 + H_2O = 2H_2SO_4 + N_2O_3.$$

The formation of these crystals, therefore, indicates that the process is not working well and more water has to be introduced.

Manuf. of Sulphuric acid by the Chamber Process :

This process uses sulphur dioxide produced by burning either sulphur or sulphide without further purification. The theory is the same as in the laboratory process. Sulphur dioxide is produced by burning sulphur or iron pyrites, FeS_2 in air in pyrites burners, which is then mixed with more air and with vapours of nitric acid generated by the action of sulphuric acid on nitre in nitre ovens. Nitric acid vapour breaks up into oxides of nitrogen. The mixture of hot gases is cooled partially by passing it up a tower known as Glover's tower. It then enters a lead chamber of about double the size of a large school room. (fig. 90). Stream or fine spray of water is injected into this chamber. Chemical reactions take place within the chamber leading to the formation of dilute sulphuric acid (65%). More concentrated acid attacks the lead of the chamber.

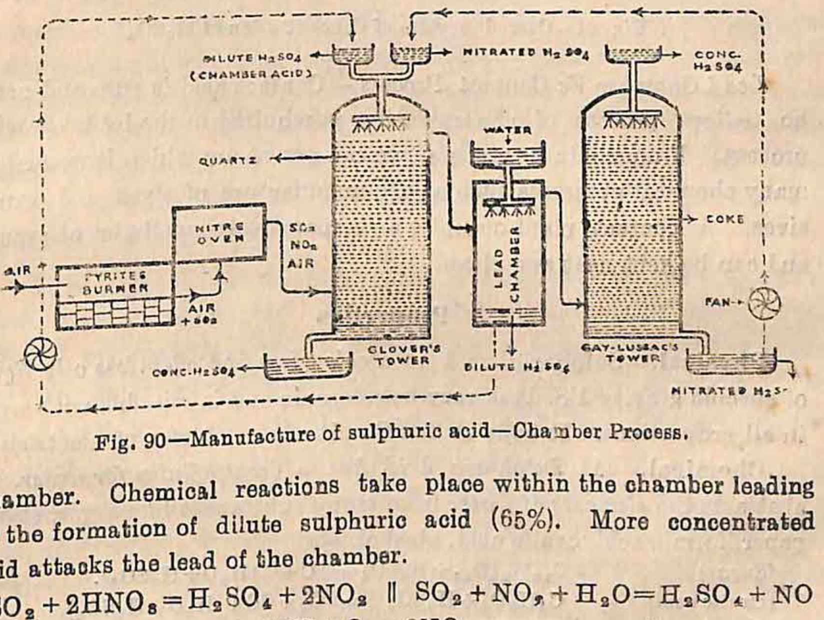


Fig. 90—Manufacture of sulphuric acid—Chamber Process.

$$SO_2 + 2HNO_3 = H_2SO_4 + 2NO_2 \quad \| \quad SO_2 + NO_2 + H_2O = H_2SO_4 + NO$$

$$2NO + O_2 = 2NO_2$$

The oxides of nitrogen are recovered from the gases issuing from the lead chamber by concentrated sulphuric acid flowing down a tower known as **Gay Lussac's tower.** The nitrated sulphuric acid thus produced and the dilute chamber acid are pumped to the top of the glover's tower and allowed to trickle down. Hot gases rising up the tower drives out the oxides of nitrogen from the nitrated H_2SO_4 to the lead chamber and also somewhat concentrates the weak chamber acid which collects at the bottom of the tower. Further concentration is done by Cascade process in which hot air is passed over dilute acid flowing down a series of pans arranged cascadewise as shown in fig. 91.

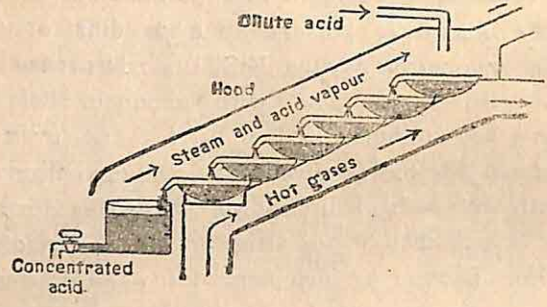


Fig. 91—Cascade system of Concentration of H_2SO_4.

Lead Chamber Vs Contact Process.—Contact acid is pure and needs no tedious process of concentration as required in the lead chamber process. From contact process, we can get oleum which is needed for many chemical processes such as the manufacture of dyes and explosives. A contact plant occupies a comparatively small plot of ground and can be kept neat and clean.

Properties

Physical.—Sulphuric acid is a *colourless* and *odourless oily liquid* of specific gravity 1·8. It is very hygroscopic and is miscible with water in all proportions. It boils at 338°C. It is a conductor of electricity.

Chemical.—(1) *Sulphuric acid has a great affinity for water.* It abstracts the *elements of water* from many substances like sugar, starch, paper, formic acid, oxalic acid, alcohol, etc.

(*Sugar*) $C_{12}H_{22}O_{11}+H_2SO_4=12C+(11H_2O+H_2SO_4)$.
(*Oxalic acid*) $C_2H_2O_4+H_2SO_4=CO_2+CO+(H_2O+H_2SO_4)$.
(*Formic acid*) $HCOOH+H_2SO_4=CO+(H_2O+H_2SO_4)$.

It mixes with water with the evolution of considerable heat, a contraction of volume taking place. If a few drops of water are added to conc. H_2SO_4, the evolved heat will convert the drops of water into steam, and due to sudden expansion, the acid will dangerously spurt.

When diluting H_2SO_4 it is always *safe*, therefore, to add *acid to water* and *not water to acid.* The acid should be gradually added to water with stirring. H_2SO_4 attacks the skin producing painful wounds.

(2) *Action of heat*—When strongly heated, it decomposes into sulphur dioxide, steam and oxygen. $2H_2SO_4=2H_2O+2SO_2+O_2$.

(3) *It acts as an oxidising agent*—Hot and conc. H_2SO_4 *oxidises* carbon and sulphur into carbon dioxide and sulphur dioxide respectively

$$C+2H_2SO_4=CO_2+2SO_2+2H_2O$$
$$S+2H_2SO_4=3SO_2+2H_2O$$

It also oxidises HI and HBr with the liberation of iodine and bromine respectively.

$$2HBr+H_2SO_4=2H_2O+Br_2+SO_2$$
$$2HI+H_2SO_4=2H_2O+I_2+SO_2$$

(4) *Action of sulphuric acid on the metal.*—Cold dilute sulphuric acid readily dissolves the metals zinc, iron, magnesium, etc. with the formation of sulphates of the metals and hydrogen. Cold *concentrated* sulphuric acid has practically *no action* on lead, mercury, tin, silver, iron etc. Hence iron vessels may be used for carrying cold conc. acid. Hot and concentrated sulphuric acid, on the other hand reacts with these metals evolving SO_2. $Cu+2H_2SO_4=CuSO_4+2H_2O+SO_2$. The metals gold, platinum, rhodium etc. are not attacked by H_2SO_4, cold or hot, dil. or conc.

Test.—(1) Dilute H_2SO_4 turns *blue* litmus-paper *red* which proves it to be acidic. (2) When heated with metallic copper, conc. H_2SO_4 evolves SO_2, which is detected by its smell of burning sulphur and *decolorisation* of $KMnO_4$ sol. (3) With $BaCl_2$ sol. it gives a white ppt. of $BaSO_4$ insol. in dil. or conc. HCl. (4) With lead nitrate solution. dil. H_2SO_4 gives a white ppt. of $PbSO_4$.

Use.—Sulphuric acid is used in the manufacture of HCl, HNO_3 and other acids ; in the manufacture of washing soda, some manures (superphosphate of lime), sulphates, explosives, paints. etc. ; in dyeing industry ; for refining petroleum ; in bleaching operations ; in making *storage* batteries or *accumulators* ; in the laboratory—for drying gases ; in the preparation of CO, ethylene, etc. Dilute H_2SO_4 is used in medicine, and also for *pickling* iron before it is galvanised.

Exercise.

1. How does sulphur occur in nature ? What are its allotropic modifications ? Give their properties and uses. *Camb., 1919 ; C. U. 1915, '23, '25, '29.*

2. Starting with roll sulphur show how you will prepare (a) SO_2, (b) SO_3 and (c) H_2S in the laboratory. What happens when each of them is brought into contact with water, and acidulated $KMnO_4$ sol. *Cam, Jun. ; Mad., 1926.*

3. How will you prepare a small quantity of H_2SO_4 in the laboratory according to the Chamber Process ? Give equations. Sketch the apparatus and give the uses of the acid. Since SO_3 is the anhydride of H_2SO_4, why is it not prepared by directly dissolving SO_3 in water ?

Delhi, 1945 : Camb. Jun. ; Mad. ; 1931 ; Bom. 1939 ; C. U., 1917, '22.

4. How will you prepare pure and dry sulphur dioxide ? Give a neat sketch of the apparatus used. Describe experiments to demonstrate its properties. State the action of the gas on (1) H_2S solution in water. (2) Bromine water, (3) milk-of lime, (4) dry coloured flowers, (5) solution of caustic soda, (6) concentrated HNO_3. Give equations. *Delhi., 1948 ; Punj., 1929 ; C. U., 1923. '33, '48, '51.*

5. How is H_2S obtained ? What is the action of H_2S on ferrous suiphate sol—*acidulated* and *alkaline* ? *Camb., Jun. ; Mad., 1937 ; Pat., 1925 ; Nag., 1927, '41.*

6. What gases are produced by the action of sulphuric acid on the following and under what conditions :—(*a*) carbon. (*b*) sulphur, (*c*) zinc, (*d*) HI and HBr.

7. Give outlines of the manufacture of Sulphuric Acid by Contact process. Describe with equations the action of hot and strong sulphuric acid on (*a*) copper and (*b*) charcoal.

Cal. Pre-U., 1961.

8. Give a neat sketch of Kipp's Apparatus and explain how it is used for the preparation of Sulphuretted Hydrogen in the laboratory.

Describe with equations what happens when it is passed into (*a*) acidulated ferric chloride solution, (*b*) acidulated copper sulphate solution. *Cal. Pre-U., 1963*

9. Give outlines of the manufacture of Sulphuric Acid by Contact Process. Describe with equations the action of concentrated sulphuric acid upon copper and the action of dilute sulphuric acid upon zinc. *Cal. Pre-U., 1963.*

10. How is Sulphuretted Hydrogen prepared in the laboratory ? Give a neat sketch of the apparatus you would use. Describe its properties and uses as a reagent.

Cal. Pre. U., 1964.

11. State with equation what happens when Hydrogen Sulphide is passed into Chlorine water.

Cal. Pre-U , 1965.

12. Describe how you would prepare pure and dry Sulphur Dioxide in the laboratory. Give a neat sketch of the apparatus used.

Describe with equations what happens when the gas is passed into : (*a*) Bromine-water, (*b*) Sodium Carbonate solution, (*c*) H_2S solution in water.

Cal. Pre-U., 1966.

13. State briefly under what conditions and with what results Sulphur Dioxide and Oxygen react together.

Cal. Pre-U., 1966.

CHAPTER XX

CARBON AND ITS COMPOUNDS

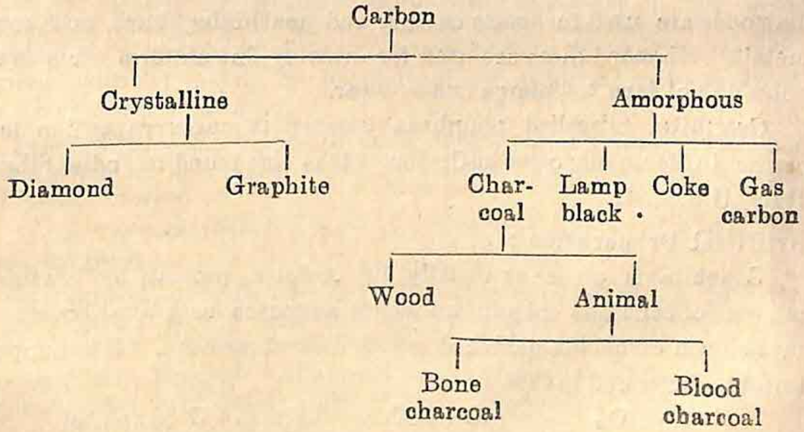
Carbon

Symbol, C At. wt., 12 At. No., 6.

Occurrence—Carbon does not occur in the free state except as graphite (also known as plumbago) and diamond. Coal is not wholly free from carbon as it is sometimes mistakenly supposed. The compounds of carbon are, however plentiful constituting the greater part of plant and animal kingdom. Substances associated closely with living matter are mostly carbonaceous compounds—marsh gas, petroleum, carbon dioxide, fats, oils, carbohydrates, proteins etc. In the mineral world, it occurs in limestone and dolomite.

Allotropic forms of Carbon :

Like oxygen, sulphur, phosphorus and many other elements, carbon is capable of occuring in several allotropic forms differing widely in their physical properties. The allotropic forms of carbon fall in two classes—crystalline and amorphous.



Diamond.—It occurs in India, Brazil, South Africa, U.S.A. and in several other places usually as octahedra or cubes, sometimes possessing perfect crystalline shapes, tinged with delightful colours such as blue, red, brown, green, pink etc. due to the presence of traces of impurities. Sometimes diamond assumes grey or black colour when it is known as carbonado or bort.

Diamond (also graphite) is supposed to be formed as a result of two great natural forces, heat and pressure acting continuously on carbonaceous materials for geological period of time.

Artificial preparation of diamond :

Moissan, a French chemist produced diamond artificially by dissolving sugar charcoal in a crucible in molten iron raised to temperature of 4000°C in an electric furnace and then plunging it suddenly in a bath of water. A portion of the carbon crystallises out due to high pressure developed in the form of small crystals of diamond and graphite which are separated from the mass of iron by dissolving the latter in hydrochloric acid.

Properties.—In the pure state, diamond is a colourless, lustrous crystalline substance. It is the hardest substance known. It is insoluble in all liquids. It owes its brilliance to its high refractive index being higher than that of any other substance. When heated strongly in air it burns to carbon dioxide. It is a non-conductor of electricity.

Uses.—It is used as a gem. Diamonds which by reason of their colour or other defects are unsuited for jewellery, are used in the cutting and polishing of precious stones and in the form of diamond drills for rock-boring and other mining operations. In industry, diamonds are used for glass cutting and machining hard and tough metals. Diamond dices are used for drawing fine uniform wires as the holes do not tend to enlarge due to wear.

Graphite, miscalled plumbago because it marks paper like lead, occurs in large deposits in Ceylon. It is also found in India, Siberia, Italy, U.S.A. etc.

Artificial Preparation :

Graphite is made artificially by *Acheson* process by heating a mixture of sand and coke in an electric furnace for several hours. At first silicon carbide is produced which decomposes at a high temperature to silicon and carbon.

$$SiO_2 + 3C = SiC + 2CO \qquad SiC = Si + C \text{ (graphite)}$$

Properties.—It is a crystalline solid like diamond but of much lower density. Unlike diamond, it is soft, dark grey in colour and is a good conductor of heat and electricity. When heated strongly it burns to form carbon dioxide.

Uses of Graphite.—Graphite (Greek *grapho*=I write) is used for the manufacture of *lead pencils*, *plumbago-crucibles*, and *electrodes* ; in making electric furnance ; in electrotyping ; in *dry cells*. It is also used as a lubricant for machinery ; as a coating for iron to prevent rusting.

Amorphous carbon is familiar to us as lampblack and various forms of charcoal obtained by burning carbonaceous matter in a limited supply of air and is known variously as wood charcoal, sugar charcoal, bone charcoal etc. according to the source from which it is derived.

(1) **Lampblack** is a pure variety of chimney soot. It is obtained on a large scale by burning some heavy oil in a closed room in which blankets are suspended from the ceiling so as to collect the soot which is deposited on it.

Lampblack finds use in the manufacture of ink, shoe polishes and black paint.

(2) **Charcoal.**—There are many varieties of charcoal of which (*a*) wood charcoal, (*b*) animal charcoal and (*c*) sugar charcoal are important.

(*a*) **Wood charcoal** is obtained by burning wood where it is plentiful in a limited supply of air in a pit or kiln. The charcoal obtained is known as 'pit charcoal'. The process is, however, wasteful.

In modern practice, wood is subjected to the process of destructive distillation by heating it in an almost closed retort. This process enable the recovery of valuable by-products. The residue in the retort is charcoal which on account of its mode of preparation is known as retort charcoal.

Properties.—Wood charcoal is a black soft substance which is actually heavier than water though it floats on the latter due to large volume of absorbed air.

It has the remarkable power of absorbing colouring matter and obnoxous gases.

(*b*) **Bone Charcoal** and *blood charcoal* are obtained by the destructive distillation of degreased bones and blood respectively. They are many times more active absorbents of gases and colouring matter. A piece of bone charcoal will absorb eighty times its volume of ammonia gas. Hence it is regularly used in sugar refineries to clarify raw sugar.

(*c*) **Sugar Charcoal** is the purest form of carbon. It is obtained by the destructive distillation of pure crystalline cane-sugar.

Coal.—Coal occurs in nature. It is a very impure form of carbon, and is said to have a vegetable origin. It is formed by the bacterial decomposition of the vegetable matter in absence of air and under great pressure of the earth. Various stages in the conversion of vegetable matter into coal are shown by the substances called *peat* (60% of C), *lignite* (70% of C), *cannel* (83% of C), *bituminous coal* (88·4% of C) and *anthracite* (94% of C).

Distillation of coal. Manufacture of coal gas :

When soft powdered coal is subjected to destructive distillation, that is heated in an almost closed retort with a narrow outlet at about

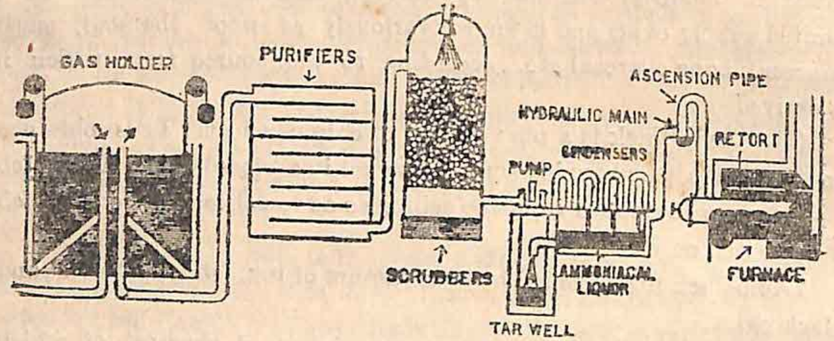


Fig. 92—Manufacture of Coal gas.

700°C—1000°C, it breaks into a number of volatile products leaving a non-volatile residue which is called coke. Some of the volatile products on cooling condense to form coal tar and ammoniacal liquor. The residual uncondensed gas is further purified from traces of NH_3, H_2S, HCN, CO_2, CS_2, etc. by washing it with water in a scrubber and leading it through a purifier containing lime and hydrated ferric oxide on alternate shelves. (fig. 92).

After purification it is stored over water under pressure in gas holders, from where it is sent as coal gas through pipes to consumers for use as a fuel. Coal gas is mainly a mixture of hydrogen (about 50%), marsh gas (30%), carbon monoxide (10%) and impurities.

During distillation of coal various by-products are obtained, the names and uses of which are enumerated below.

(1) **Coal-tar.**—It is a black, foul-smelling, viscid liquid ; a mixture of a large number of organic compounds.

Use.—It is used (i) for preserving timber ; (ii) making tarred paper ; and (iii) in the manufacture of benzene, carbolic acid, etc.

(2) **Ammonia.**

(3) **Gas-lime or Spent-lime** obtained from the purifiers is used as manure.

(4) **Coke.**—It is the substance left in the retorts after the destructive distillation of coal. **Use.**—It is used as valuable fuel and in metallurgy.

(5) **Gas-Carbon.**—It is formed as a hard, dense deposit on the inner side of the retorts. Use.—It is used as electrodes in electric furnaces, in electric cells and in arc lamps.

(6) **Spent oxide of Iron.**—It is sometimes used for generating SO_2 required in the manufacture of H_2SO_4.

Oxides of Carbon

Carbon dioxide, CO_2 : Carbon monoxide, CO.

Carbon dioxide

Formula, CO_2. Mol. wt., 44 Density, 22.

Occurrence—Carbon dioxide occurs in nature. Air contains free carbon dioxide. It is a product of combustion of fuel and respiration of animals. It is also found in solution in all spring water, which is sometimes so highly *charged* with the gas, under pressure, that the water is effervescent or 'sparkling', due to the escape of dissolved CO_2. It also issues in abundance from the earth in certain localities.

In combination with lime it occurs very abundantly in **calcite, chalk, marble, limestone**; and with magnesia in **magnesite.** Processes of fermentation etc. also produce carbon dioxide.

Preparation.—Carbon dioxide is obtained—

(1) *By the combustion of Carbon and its compounds*—We get carbon dioxide when carbon is burnt in *excess* of air or oxygen. $C + O_2 = CO_2$.

If there is an insufficient supply of air or oxygen, carbon monoxide is also produced.

(2) *By the action of heat on carbonates and bicarbonates.*

$$CaCO_3 = CaO + CO_2$$
$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2$$

(3) *By the action of acids on carbonates.*

Laboratory Method :—

Place small pieces of marble in a Woulfe's bottle fitted with a thistle funnel and a delivery tube (fig. 32). Now pour dilute hydrochloric acid down the funnel taking care to see that the end of the funnel dips into the liquid. At once there is an effervescence and carbon dioxide gas is evolved. Collect the gas by the *upward* displacement of air. $CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2$.

N. B.—(i) The gas, thus prepared, contains *free* HCl. To remove it, the evolved CO_2 is passed through sodium bi-carbonate solution (which reacts with HCl, but not with CO_2) ; it is then bubbled through conc. H_2SO_4 and is collected over mercury. The gas is now *fairly pure* and *dry*.

(ii) It is easy to test if a jar is full of CO_2—Insert a lighted taper into the jar of CO_2. The taper is extinguished as completely *as if it has been immersed in water*.

(iii) Sulphuric acid also decomposes $CaCO_3$ giving off CO_2. But it is not used for that purpose, for the *sparingly soluble* $CaSO_4$ produced forms a coating on marble. This prevents the marble from coming in contact with the acid, and the action consequently ceases. As calcium chloride is highly soluble, no such difficulty arises when HCl is used. $CaCO_3 + H_2SO_4 = CaSO_4 + H_2O + CO_2$.

Manufacture—On a large scale, carbon dioxide is obtained as a by-product—(a) during the manufacture of lime (*lime-kiln gases*); (*b*) during the fermentation of sugar solution by yeast (brewing industry); (*c*) by the action of sulphuric acid on magnesite or on sodium carbonate; and (*d*) from furnace gases.

Properties : Physical —Carbon dioxide is a *colourless* gas with a faint acid taste and smell. It is not poisonous, but animals cannot live in it, for they are suffocated from lack of oxygen. It is heavier than air. The gas is fairly soluble in water at the ordinary temp. ; 1 vol. of water dissolves 1 vol. of the gas. The solubility of carbon dioxide is considerably increased by the increase of pressure. Soda water and other aerated waters contain this gas dissolved in water under pressure. The whole of the gas can be expelled by boiling the solution. The aqueous solution possesses *feebly acidic properties* ; for it turns litmus solution *port-wine* colour *possibly* owing to the formation of the weak *carbonic acid*, which, however, has not been isolated. $CO_2 + H_2O = H_2CO_3$.

The gas can be liquefied to a colourless liquid in which condition it is transported in industry in steel cylinders.

Chemical—Carbon dioxide is in general a non-supporter of combustion and of animal life. But it supports the combustion of *burning* magnesium with the liberation of carbon.

$$2Mg + CO_2 = C + 2MgO.$$

It reacts with alkalis giving alkali carbonates which is converted by more CO_2 into alkali bi-carbonates It turns lime-water milky, owing to the formation of insoluble calcium carbonate which dissolves when excess of carbon dioxide is passed into the liquid due to the formation of calcium bi-carbonate.

$$2KOH + CO_2 = K_2CO_3 + H_2O$$
$$K_2CO_3 + H_2O + CO_2 = 2KHCO_3$$
$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$$
$$CaCO_3 + H_2O + CO_2 \rightleftharpoons Ca(HCO_3)_2.$$

When passed over red-hot carbon it is reduced to carbon monoxide.

$$CO_2 + C = 2CO.$$

CO_2 is decomposed by the green colouring matter of plants ; in presence of sunlight. Carbon is assimilated and oxygen is set free.

Liquid and Solid carbon dioxide.—CO_2 condenses to a mobile liquid when subjected to a pressure of about 40 atmospheres at 0°C. When liquid CO_2 is allowed to evaporate, a portion of it is frozen into a soft, white, snow-like substance called 'Carbonic acid snow' or Dry ice or Drikold.

Test—(i) CO_2 extinguishes a burning taper ; (ii) when CO_2 is passed into lime-water or a glass rod dipped into lime-water is held in the gas, the lime-water turns milky.

Absorbents.—NaOH, KOH, $Ca(OH)_2$, etc

Use.—CO_2 is used in the manufacture of aerated waters like soda-water, lemonade, etc. : in extinguishing fire ; in the manufacture of sugar, sodium carbonate, salicylic acid, etc. : *liquid* and *solid* CO_2 are used as refrigerating agents.

Carbon dioxide Cycle in Nature—All living creatures, animals and plants breathe in oxygen during inhalation and breathe out carbon dioxide during exhalation. The combustion of fuel and decay of organic matter are also using up the oxygen of the air to produce carbon dioxide gas which is continually finding its way into the atmosphere. The proportion of oxygen in air tends to decrease and that of carbon dioxide to increase till, if the process were allowed to continue undisturbed, there would be too little oxygen in the air to sustain life on earth. Fortunately a reverse process known as photosynthesis is going on simultaneously which maintains the ratio of the amount of oxygen and carbon dioxide almost constant in air. During photosynthesis, all green plants with the help of the energy derived from diffused or direct sun-light and in presence of the green colouring matter of leaves (*chlorophylls*) absorb carbon dioxide gas from the air, assimilate the carbon and give back oxygen to the air. This assimilation of carbon dioxide is believed to take place in two stages. At first formaldehyde is produced and an equal volume of oxygen is set free for every one volume of carbon dioxide absorbed.

$$CO_2 + H_2O = \underset{\text{formaldehyde}}{H.CHO} + O_2.$$

Formaldehyde then polymerises into sugar, starch, cellulose etc.

Thus the two processes are going on simultaneously—respiration and photosynthesis, one reverse to the other to keep the percentage of carbon dioxide more or less constant in the air. This is known as carbon dioxide cycle.

The Molecular formula of Carbon dioxide

The molecular formula of carbon dioxide can be derived from its volumetric composition with the help of Avogadro's hypothesis. It can be shown by burning a piece of pure carbon in a given volume of oxygen over mercury in the closed limb of a U-shaped eudiometer tube that after the combustion of carbon, no change in volume takes place, when measured at the same temperature and pressure. This shows that carbon dioxide gas contains its own volume of oxygen, i.e., one volume of carbon dioxide contains one volume of oxygen.

Let one volume of oxygen contain n molecules of oxygen, then one volume of carbon dioxide will also contain n molecules of carbon dioxide (by Avogadro's hypothesis).

Hence,

n molecules of carbon dioxide contain n molecules of oxygen.

Or, 1 molecule of carbon dioxide contains 1 molecule of oxygen, or 2 atoms of oxygen ($\because$ oxygen molecules are diatomic).

$\therefore$ the molecular formula of carbon dioxide is C_xO_2 (x unknown).

Now the vapour density of carbon dioxde is 22.

Therefore, its mol. wt. $= 2 \times 22 = 44$ (by Avogadro's hypothesis)

Hence, $C_xO_2 = 44$ or $12x + 32 = 44$ or $12x = 12$ or $x = 1$

Hence, the molecular formula of carbon dioxide is CO_2.

Carbon monoxide

Formula, CO Mol. wt., 28 Density, 14.

Occurrence.—This gas seldom occurs free in nature. Only minute traces have been detected in air in the vicinity of volcanoes. It is found in tobacco smoke, in chimney gases where the supply of air is not sufficient, in coal-gas and in the gases from *blast* and other furnaces.

Preparation : (1) From Carbon dioxide.—Carbon monoxide is formed when carbon dioxide is passed over charcoal heated to bright redness. $CO_2 + C = 2CO$.

Carbon monoxide is also formed by the reduction of CO_2 when it is passed through a tube containing *red-hod* metals like iron, zinc, etc.

$$4CO_2 + 3Fe = Fe_3O_4 + 4CO ; Zn + CO_2 = ZnO + CO.$$

(2) **From Carbon.**—When steam is passed over *white-hot* coke, a mixture of carbon monoxide and hydrogen (*water gas*), containing a *small* amount of CO_2 is produced.

$$C + H_2O = \underbrace{CO + H_2}_{\text{Water gas}}.$$

(3) **From Organic compounds, Laboratory method.**—CO is best prepared in the laboratory by (i) abstracting the elements of water from (*i.e.*, by *dehydrating*) formic acid or (ii) oxalic acid by conc. H_2SO_4.

(i) **From Formic acid.**—Heat conc. sulphuric acid to about 100°C in a flask clamped to a retort stand and provided with a dropping funnel and a delivery tube. Now carefully drop formic acid from the funnel upon the sulphuric acid. Conc. H_2SO_4 abstracts the elements of water from formic acid, and carbon monoxide is evolved. Collect the gas over water.

$$H.COOH + [H_2SO_4] = CO + [H_2O + H_2SO_4]$$

Pure CO.—Carbon monoxide may, however, contain a trace of SO_2. To get it *absolutely* pure and dry, pass the gas first through KOH solution, then through P_2O_5 and finally collect it over mercury.

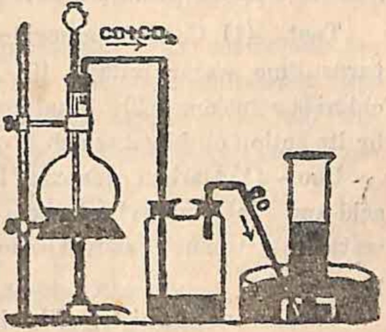


Fig. 93—Prep. of CO from oxalic-acid.

(ii) **From Oxalic acid.**—Introduce crystallised *oxalic acid* into a flask, clamped to a retort stand and fitted with a thistle funnel and a delivery tube. Pour concentrated sulphuric acid down the funnel so that the end of the funnel dips under H_2SO_4. Now heat the flask *gently* on a piece of wire-gauze. Effervescence sets in with the evolution of carbon monoxide and carbon dioxide. Pass the issuing gases through a Woulfe's bottle containing caustic potash solution in which CO_2 is absorbed, but not CO (fig. 93). Collect carbon monoxide over water. $H_2C_2O_4+[H_2SO_4]=CO_2+CO+[H_2O+H_2SO_4]$

Properties : Physical.—Carbon monoxide is *a colourless, tasteles* gas with a peculiar faint smell. It is very slightly soluble in water, and is nearly as heavy as air. The gas condenses to a colourless, transparent liquid boiling at −191°C.

Chemical.—Carbon monoxide is combustible, and does not support combustion. It burns in air with a *lambent blue* flame forming carbon dioxide. When mixed with oxygen and inflamed, it explodes violently. It is an *unsaturated* compound and combines directly with chlorine, in sunlight, to form *carbonyl chloride* or *phosgene gas* which is highly poisonous, $CO+Cl_2=COCl_2$. Finely divided cobalt, nickel and iron unite with carbon monoxide on heating, giving compounds called '*carbonyls*' ; Nickel carbonyl—$Ni(CO)_4$, iron carbonyl—$Fe\,(CO)_5$, etc. The gas acts as a powerful reducing agent at high temperatures. Thus when passed over red-hot cupric oxide it reduces the oxide to metallic copper. $CuO+CO=Cu+CO_2$. Carbon monoxide is absorbed by a solution of cuprous chloride either in conc. HCl or in $NH_4(OH)$. It does not react with caustic soda or caustic potash solution in cold. Sodium formate, however, is formed when CO at 160°C and *under pressure* is passed into NaOH sol.

$NaOH+CO=H.COONa$ (sodium formate)

Carbon monoxide is a *very poisonous gas.* It forms a stable compound with the haemoglobin of blood. Fatal accidents have arisen from the breathing of CO issuing from fire in ill-ventilated dwelling-rooms.

Test.—(1) Carbon monoxide burns with a blue flame. The product turns lime water milky. (2) It is absorbed by ammoniacal cuprous chloride solution. (3) Small amount of carbon monoxide is detected by its action on blood which is examined spectroscopically.

Use.—(1) Carbon monoxide is used in the manufacture of (*a*) formic acid and (*b*) methyl alcohol, (2) in the form of producer gas and water gas, it is used as fuel and (3) for extraction of nickel by Mond's process.

Carbon disulphide, CS_2 is prepared by passing sulphur vapours through red-hot charcoal. It is a colourless volatile liquid, b. p., 46°C. It has when fresh, an ethereal odour which becomes disgusting after sometime. It is highly inflammable and poisonous.

Use.—It is an excellent solvent of fats, oils, sulphur, phosphorus, iodine etc. It is used to some extent as a poison against agricultural pests, but its largest single use is in the manufacture of rayon.

Exercise.

1. Name the natural and artificial forms of carbon. How are they obtained? Mention their uses.

2. How would you separate carbon monoxide from carbon dioxide in a mixture of the two? What is coke and what are its uses?

C. U., I Sc., '15, '23, '25, '30, '34, '39, '41.

3. What function does atmospheric CO_2 play in the growth of plants? Compare the gaseous compounds of carbon you have read.

C. U., 1919, '26, '27, '32, '48 ; All, 1922.

4. How is *pure* CO prepared? Write down its properties. What is the action of the gas on (a) nickel, (b) NaOH, and (c) chlorine?

Mad., 1932 : C. U. B. Sc., 1935, '41, '44, '47.

5. Explain with equations what happens when Carbon Dioxide is passed into lime water gradually to excess.

Cal. Pre-U., 1961, '62.

6. Give a brief outline of the laboratory method of preparation of carbon dioxide. State its important properties and uses.

Cal. Pre-U., 1961.

7. Name the important products that are obtained when coal is subjected to destructive distillation. State their uses.

Cal. Pre-U., 1962.

8. State with equations what would happen when Carbon Dioxide is passed through red hot Carbon.

Cal. Pre-U., 1964.

9. You have been supplied with three jars containing ammonia, carbon dioxide and hydrochloric acid gas. State how you would identify these gases.

Cal. Pre-U., 1965.

10. What happens when:

(*a*) Carbon Dioxide is continuously passed into lime water.

(*b*) A burning Magnesium ribbon is introduced into a gas jar full of Carbon Dioxide and the products thus obtained are shaken with dilute Hydrochloric acid.

Cal. Pre-U., 1967.

CHAPTER XXI

METALS

Having finished the study of non-metals and their compounds we are about to begin the study of metals and their compounds ; but before we do so, let us see in what respects metals differ from non-metals. Some of the distinguishing properties of these two classes of elements are tabulated below.

Distinctions between Metals and Non-Metals

(A) Distinctions based on Physical Properties.

Metals	Non-Metals
1. *Metals possess a lustre called metallic lustre*	1. *Non-Metals do not possess any metallic lustre.*

Exception.—Non-metals like **Iodine** and **Graphite** possess metallic lustre. Therefore, this distinction fails in their cases.

2. *Metals are electro-positive.*	2. *Non-Metals are generally electro-negative.*

Exception.—**Hydrogen**, though a non-metal, is *electro-positive.* Therefore, this distinction breaks down here. Metals are also sometimes found present in *complex negative radicals like* $Fe(CN)_6$, etc.

3. *Metals are generally good conductors of heat and electricity.*	3. *Non-metals are poor conductors of heat and electricity.*

Exception.—**Graphite**, a non-metal, is a good conductor of electricity ; and **hydrogen**, also a non-metal, is a good conductor of heat (as compared with other gases). They are, therefore, exceptions to the above rule.

4. *Metals are generally solids at the ordinary temperature.*	4. *Non-metals are gases and solids at the ordinary temperature.*

Exception.—**Mercury**, a metal, is a **liquid** at the ordinary temperature ; and **bromine**, a non-metal, is also a liquid at the ordinary temperature.

5. *Metals are malleable and ductile ; have high specific gravities ; and reflect light*	5. *Non-metals are not malleable and ductile ; have low specific gravities ; and do not reflect light.*

Exception.—**Sodium** and **potassium** have specific gravities less than that of water. **Plastic sulphur** is ductile to some extent ; and **bismuth** is brittle.

6. *Metals when struck with a hammer, emit a peculiar sound, called metallic clink.*	6. *Non-metals do not emit a metallic sound.*

(B) Distinctions based on Chemical Properties.

7. *Oxides of metals are basic.*	7. *Oxides of non-metals are acidic.*

That is to say, the oxides of metals neutralise acids to form salts and water; the oxides of non-metals like sulphur, phosphorus, nitrogen, etc. react with water to give acids. Oxides of some metals like sodium, potassium, calcium, etc. react with water to form *strong* bases or *alkalis*.

$$Na_2O + H_2O = 2NaOH \qquad SO_3 + H_2O = H_2SO_4$$

Exception.—Zinc, aluminium, tin, etc. form oxides which are also acidic in character; and they form salts, like the zincates, aluminates; stannates etc. with alkalis. Some non-metallic oxides like NO. water, etc. are *neutral*. Therefore, this distinction is not always tenable,

8. *Metals frequently dissolve in dil. mineral acids giving off hydrogen.*	8. *Non-metals usually do not dissolve in dil. acids.*

Exception.—Some metals do not give off hydrogen when treated with an acid under ordinary circumstances.

9. *Metals either do not combine with hydrogen at all or form non-volatile, unstable hydrides.*	9. *Non-metals form stable compound with hydrogen.*
10. *Metallic chlorides are not decomposed at all or only partially by water.* $NaCl + H_2O \rightarrow$ No *Hydrolysis* $AlCl_3 + 3H_2O \rightleftharpoons Al(OH)_3 + 3HCl.$	10. *Non-metallic chlorides are often decomposed by water completely.* $PCl_3 + 3H_2O = 3HCl + H_3PO_3$ $SiCl_4 + 4H_2 = Si(OH)_4 + 4HCl.$

Introduction to the study of Metals

The high tensile strength, malleability, ductility etc. of metals—the properties lacking in non-metals, have proved of very great use to man.

Infinitely better tools, implements and weapons of offence and defence could be fashioned out of metals than the rough ones which could be hewn out of stones and these gave our early ancestors a decisive superiority over the animal world with which in those early days they were engaged in mortal struggle for their survival. In fact, the discovery of metals placed man well on the road to civilisation and material prosperity. The metals, indeed, form the very basis of the modern mechanised civilisation of ours with its metal-made machines and tools.

The importance of metals on the growth of civilisation can be very well gauzed from the fact that historians have named the successive periods of human civilisation as bronze age, iron age etc.

The erection of iron and steel factories has been given the top priority in India's planned economy, for the various development projects which would provide reasonable happiness to the teeming millions of India's population, are dependent on the adequate production of iron and steel within the country.

Besides the existing older iron and steel factories, three others (at Rourkella, Villai and Durgapur) have been erected under the auspices of India's Second Five Year Plan and recently they have been commissioned into operation, each having the productive capacity of more than a million ton of steel a year.

India is peculiarly fortunate that she possesses a huge deposit of iron ores along with coal, limestone and manganese—the very materials required for the production of iron and steel—in closer proximity with one another, than, perhaps, anywhere else in the world.

India produces more manganese than she can consume within her borders. So she exports the surplus for the much needed foreign exchange.

Aluminium is another metal of which India possesses huge deposits in the form of bauxite—an oxide of the metal from which the metal can be easily extracted. There are several factories in India now which are exploiting bauxite for the metal. Some more are under way and in near future will go into actual operation. India has also significant deposits of copper and gold. The former occurs as a mineral in the Singhbhum district of Bihar and the latter in Kolar gold fields near Mysore. India has also a rich store of radio-active minerals—uranium and thorium, the latter occuring as monazite in large quantities in Travancore. These minerals when harnessed will provide India with cheap atomic energy for the development of her backward economy.

Occurrence.—Metals do not occur as a rule in the uncombined state, i.e, free or as we say **native** in nature. Only a few metals, gold, platinum, silver and to a much lesser extent copper—metals which are very low down in the activity series are found native. Metals occur in the form of minerals or compounds embedded in a matrix of rocky matter. The whole of the mineral is not necessarily composed of the metallic compound, the proportion of which may not exceed more than a few per cent only, the rest being worthless rocky matter which is called the **gangue**. Even such poor minerals have been successfully worked for the metals. Minerals from which the metal can be extracted profitably is called the **ore** of the metal. Thus bauxite is an ore of aluminium, for the metal aluminium is obtained chiefly from it; whereas clay which also contains aluminium, is not an ore of the metal because uptil now no method has been discovered for extracting aluminium profitably from it. Most of the heavier metals occur as (1) oxides, (2) sulphides and (3) carbonates. Metals like potassium, sodium, calcium, magnesium etc, which are at the top of the activity series do not occur either as oxides or sulphides, because the oxides and sulphides of these metals are readily decomposed by air and water. These are found generally as *chlorides*, *sulphates*, *nitrates* and also as *carbonates* and *bicarbonates* in sea water and as underground deposits.

Metallurgy.—Winning a metal from its ore which is known as *metallurgy* is quite often not an easy task, for it involves (1) the separation of mechanical impurities (gangue) as far as possible as well as (2) removing the elements which are found combined chemically with the metals.

(1) The first process (concentration of the ore) is generally effected by gravity separation. The crushed ore is washed with water when the metallic compounds on account of their high specific gravities tend to fall to the bottom, whereas the lighter gangue rise up with water and is washed away.

Where such separation is found impracticable, the concentration of the ore (particularly if it is a sulphide) is accomplished by *oil floatation process.* The finely powdered ore is mixed with oil and water and other reagents and air is blown into it. A large quantity of froth is produced. The oil wets the sulphide ore which, therefore, rises with the froth produced, whereas water wets the gangue (silica) and carries it down. The froth is afterwards allowed to die. The oil is separated and used again.

Magnetic separation is sometimes resorted to when other methods fail to remove magnetic impurities such as wolfram from tinstone.

(2) The second process involves reduction of the concentrated ore by a suitable reducing agent.

(A) Reduction by Carbon or Carbon Monoxide

In the case of commoner metals—Iron, zinc, lead etc., the reduction is usually effected by carbon and carbon monoxide. Sometimes in the case of less reducible metals such as manganese and chromium, the reduction is effected by the metal aluminium (*Alumino thermic process*). Before reduction, the ore is to be converted into an oxide, if not already so, by the process of *roasting* or *calcining*.

Calcination and Roasting.—These two terms are used, somewhat interchangeably, among the metallurgists though a distinction *may* be made between them.

Roasting.—To roast a substance is to heat it at a temp. insufficient to melt it (*i.e. below* the point of *fusion*) but *always* in presence of air with a view to *oxidising* it. The term is usually applied to the case of ores.

Example.—Zinc blende (ZnS) is roasted in air to convert it into zinc sulphate, $ZnSO_4$,

Calcining.—To calcine a substance is to heat it very strongly but at a temperature insufficient to melt it, with a view to driving off volatile matters.

Example.—(1) Oxide ores are preliminarily calcined to remove moisture and other volatile impurities. (2) Limestone or dolomite is *burnt* in kilns to expel CO_2.

Roasting and calcining and as a matter of fact many of the metallurgical operations at high temperatures are brought about in a *reverberatory furnace.*

Reverberatory Furnace.—This is a special type of furnace much used in metallurgy. Here the substances are heated not directly over the fire, but by the hot gases produced in the fireplace. The furnace is made of fire-bricks and is provided with walls on all sides. The fireplace is built at one end of the structure at a level slightly lower than that of the furnace (*i.e.*, hearth) which is separated by two small walls from the fireplace and the flue leading to the chimney. The roof is low and is usually made *slanting* so that the hot gases from the fireplace are *reverberated* or *reflected* by the roof over the hearth. Air can enter through the iron grates of the fireplace. There are doors in front of the furnace for introducing and working the charge, as also tap-holes on the other side to take out the charge. (fig. 94).

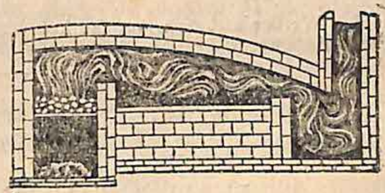


Fig. 94—Reveberatory furnace.

Flux.—Gangue which is generally infusible at the temperature at which the metal is extracted must be removed, as on account of its infusibility it tends to remain embedded in the metal and it would be very difficult to eliminate them later on. Hence suitable substances called *flux* are added (a base such as lime or limestone if the gangue is of acidic nature or an acidic substance such as silica if the gangue is basic) so that the flux and the gangue may combine to form a substance (slag) which melts and forms a layer on the top of the molten metal. The metal and slag are separated through separate holes. The crude metal generally requires further purification.

Slag.—The fusible *compound* formed by the union of the 'flux' and the 'impurities' especially when it is the waste product of an operation, is termed 'slag'. Slag=flux+impurities.

Alloy—An alloy is a *mixture* or compound or both of two or more metals. When one of these two metals happens to be Mercury, the alloy is called an amalgam.

Amalgam—An amalgam is an alloy of Mercury with other metal or metals.

(B) Reduction by Electrolysis

With metals like potassium, sodium, calcium etc, which occupy top positions in the activity series, it is very difficult to win the metal by carbon reduction process. Here reduction of the ore (generally a chloride) is effected by electrolysis in the molten state.

Exercise.

1. Distinguish a metal from a non-metal. Draw a neat sketch of the riverberatory furnace.

2. Could you extract calcium from CaO by the carbon reduction method? If not, why not?

3. Write short notes on the following terms: (a) Slag; (b) Roasting; (c) Alloy; (d) Basic Slag.
Cal. Pre-U. 1970

CHAPTER XXII

ALKALI METALS AND THEIR COMPOUNDS

The metals like sodium, potassium etc. are called alkali metals because they occur in substances like sodium carbonate, potassium carbonate etc., which have been long known as alkalis.

Sodium

Symbol, Na At. wt., 23 At. No, 11

Occurrence—Sodium metal does not occur free in nature. It however, occurs abundantly as,

(1) Chloride which is obtained from sea water as common salt and from mines as *rock salt*.

(2) Nitrate; huge deposits occur and are mined in Chili as *chili saltpetre*.

(3) Carbonate found in several countries as an efflorescent solid—for example as *sajimati* in India and *trona* in Egypt.

Extraction—Sodium metal can be obtained from sodium carbonate by heating it strongly with charcoal.

$$Na_2CO_3 + 2C = 2Na + 3CO$$

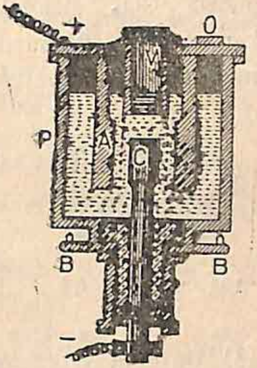
Commercially, however, it is now-a-days obtained exclusively by electrolytic processes.

Two different processes are employed—

(1) *Castner's process* which is older of the two, uses molten caustic soda and (2) *Downs' process* which is very recent, obtains the metal directly from sod. chloride.

Castner's Process—

In this process, Caustic Soda is melted in an iron vessel (P) and kept at a temperature not above 330°C by a ring of gas flames (BB). It is electrolysed with an iron cathode and a nickel anode.



Fig, 95—Extraction of Sodium-Castner's process

The iron cathode (C) which is an iron rod is introduced from the bottom and is kept in an erect position by allowing the molten caustic soda in the lower part of the vessel to solidify.

The nickel anode which is a cylinder made of nickel is suspended from the ceiling from which it is, however, insulated by special means. It surrounds the iron cathode.

On electroysis, sodium and hydrogen are set free at the cathode and collect inside an iron box placed above the cathode. Sodium is removed from time to time by means of perforated spoons which retain the metal but allow the molten caustic soda to flow back. Oxygen is set free at the anode and escapes through an outlet (O). (Fig. 95).

$$2NaOH = \underbrace{2Na + \uparrow H_2}_{cathode} + \underset{anode}{\uparrow O_2}$$

Down's process—In this process, sodium metal is obtained by the electrolysis of molten sodium chloride with iron cathode and carbon anode.

$$2NaCl = \underset{cathode}{2Na} + \underset{anode}{\uparrow Cl_2}$$

Properties

Physical—Sodium is a *silver-white* metal. It can be cut with a pen-knife and pressed between the fingers. Its sp.gr. is 0'97. Hence it is lighter than water and floats on it.

Chemical—(1) *Action of air or oxygen*—Perfectly *dry* air or oxygen is without action upon sodium. Moist air tarnishes it superficially owing to the deposit of a film of the monoxide, which now reacts with the moisture of air giving caustic soda. NaOH then absorbs atmospheric CO_2 yielding Na_2CO_3. Sodium is therefore, kept under kerosene oil. It burns in air or in oxygen with a *golden-yellow* flame producing a mixture of sodium monoxide and sodium peroxide.

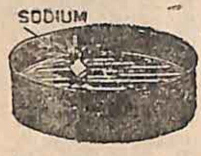


Fig. 96—Na with water.

(2) *Action of water*—Sodium decomposes water at the ordinary temp. to form caustic soda and hydrogen. $2Na+2H_2O=2NaOH+H_2$. It being lighter than water, all the time it decomposes water, it floats on the surface of water. (3) *Action of halogens*—Sodium, when heated in Cl_2 burns with a bright yellow light giving NaCl. (4) Burning Na decomposes CO_2 setting carbon free and producing sodium carbonate. $4Na+3CO_2=2Na_2CO_3+C$. (5) When heated in dry hydrogen at 365°C sodium hydride, NaH is formed. $2Na+H_2=2NaH$. It forms an *Alloy* with potassium which is a liquid at the ordinary temp. With mercury it forms an *amalgam* which evolves hydrogen when acted upon by water. (fig. 96).

Uses of Sodium.—Sodium is used in the manufacture of sodium peroxide, sodium cyanide ; for the extraction of boron and silicon ; an alloy of sodium and potassium is used in high temp, thermometers above the boiling-point of mercury ; sodium amalgam is used as a reducing agent. Sodium is also used in the laboratory for detecting different elements present in organic compounds.

Oxides of Sodium

There are two oxides of sodium—(i) sodium monoxide and (ii) sodium peroxide.

Sodium monoxide, Na_2O is formed when sodium metal is heated in a limited supply of air at 180°C. $4Na+O_2=2Na_2O$. It is a grey powder which reacts with water to produce caustic soda.

$$Na_2O+H_2O=2NaOH$$

Sodium Peroxide, Na_2O_2 is prepared by heating metallic sodium in excess of purified air at 300°C on aluminium trays.

$$2Na+O_2=Na_2O_2.$$

It is a yellowish white solid. With water, it liberates oxygen,

$$2Na_2O_2+2H_2O=4NaOH+O_2$$

With ice cold and dilute sulphuric acid, it gives hydrogen peroxide

$$Na_2O_2+H_2SO_4=Na_2SO_4+H_2O_2.$$

Use.—Sodium peroxide is used as a bleaching agent—for bleaching silk, wool, straw, and other delicate stuffs which cannot be bleached by chlorine : for preparing oxygen ; as an oxidising agent in the laboratory ; and in dyeing industry.

Sodium hydroxide, Caustic soda, NaOH.—It may be obtained by the action of water on metallic sodium or sodium monoxide or sodium peroxide.

Commercially, it is obtained by (1) the electrolysis of sodium chloride solution and (2) by causticising sodium carbonate solution by lime.

(1) Caustic soda by the electrolysis of the sodium chloride solution.

Theory.—Sodium chloride solution in water contains Na^+ ions and Cl^- ions. Water is also ionised to some extent and furnishes H^+ ions and OH^- ions. On electrolysis, the H^+ ions are discharged at the cathode and Cl^- ions at the anode leaving Na^+ ions and OH^- ions in the solution. These are the components of caustic soda. The solution on evaporation furnishes solid caustic soda which is fused and cast into sticks, balls etc.

$$\begin{array}{l} 2Na^+Cl^- = 2Na^+ + 2Cl^- \\ 2H_2O \quad = 2H^+ + 2OH^- \\ 2H^+ + 2e = H_2 \\ 2Cl^- \quad = Cl_2 + 2e \\ \hline 2Na^+Cl^- + 2H_2O = \underbrace{2Na^+ + 2OH^-}_{\text{Caustic soda}} + H_2 + Cl_2 \end{array}$$

Chlorine which is set free at the anode must not be allowed to come in contact with caustic soda, for it will react with the latter. In that case caustic soda produced would be impure. This difficulty is got over by using (a) mercury cathode cells or (b) diaphragm cells.

Mercury Cathode Cell—Kellner Solvay Cell

These cells give caustic soda of high purity, but are expensive because a large quantity of costly mercury is required.

Kellner-Solvay Cell.—(Modified Castner Kellner's method). The Kellner-Solvay cell consists of a number of graphite carbon anodes suspended in a flowing stream of brine. Below the brine and flowing slowly in the same direction along the base of the cell is a thin layer of mercury which is made the cathode (fig. 97). On passing electric current, chlorine is discharged at the anode (some remains in solution).

Sodium discharged on the mercury cathode forms an amalgam with it and collects in a lower tank where it is decomposed by water in presence of metallic iron. When the strength of caustic soda formed reaches 40%, it is withdrawn, evaporated and the solid caustic soda obtained is melted and cast into sticks or allowed to solidify in iron drums.

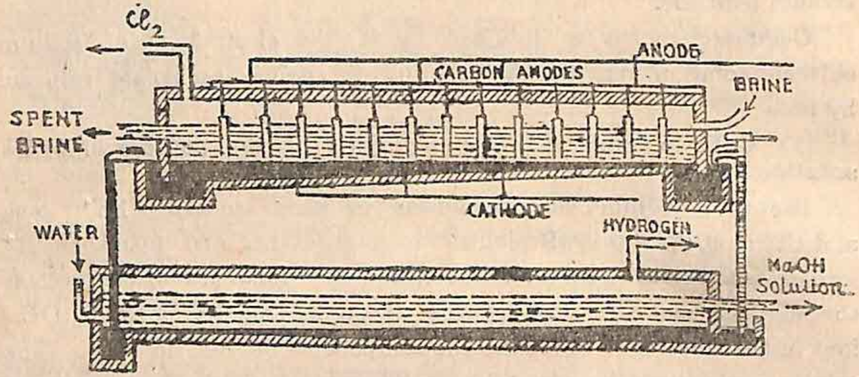


Fig. 97—Kellner-Solvay Cell.

In the Primary Cell

$$\begin{aligned}2NaCl &= 2Na^+ + 2Cl^- \\ 2Cl^- &= Cl_2 + 2e \\ 2Na^+ + 2e &= 2Na \\ \hline 2NaCl &= 2Na + Cl_2\end{aligned}$$

In the Decomposer

$$\begin{aligned}2H_2O &= 2H^+ + 2OH^- \\ 2Na &= 2Na^+ + 2e \\ 2H^+ + 2e &= H_2 \\ \hline 2Na + 2H_2O &= 2Na^+ + 2OH^- + H_2 \\ & \quad (2NaOH).\end{aligned}$$

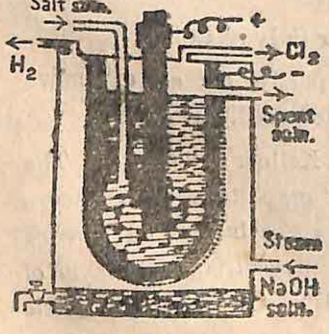


fig. 98—Nelson Cell

Diaphragm Cell

One important cell of this *type* is *Nelson Cell.* The carbon anode dips in brine within a perforated steel cylinder serving as cathode. A porous asbestos diaphragm separates the anode from the cathode. They are enclosed within a bigger vessel with outlets for the escape of gaseous products. (fig. 98). On electrolysis, sodium is set free at the cathode in the outside compartment and is converted by steam into caustic soda and hydrogen.

$$\begin{aligned} 2Na^+Cl^- &= 2Na^+ + 2Cl^- \\ 2Na^+ + 2e &= 2Na \\ 2Na + 2H_2O &= 2NaOH + H_2 \\ 2Cl^- &= Cl_2 + 2e \\ \hline 2Na^+Cl^- + 2H_2O &= 2NaOH + H_2 + Cl_2 \end{aligned}$$

Chlorine liberated at the anode is led away through an outlet.

(2) **Caustic soda from sod. carbonate by lime.**—A solution of soda-ash in water of 20% strength is heated to boiling, by means of steam, with milk-of-lime in tanks fitted with stirrers. By double decomposition, sodium hydroxide and $CaCO_3$ are formed.

$$Na_2CO_3 + Ca(OH)_2 = CaCO_3 + 2NaOH,$$

The insoluble calcium carbonate is allowed to settle. The solution contains caustic soda. The clear solution of sodium hydroxide is now drawn off and evaporated to dryness in iron vessels, when solid caustic soda is obtained. It is usually melted down and then cast into sticks.

Properties—Caustic soda is a white crystalline, highly deliquescent solid. It melts at 318°C and *dissociates* into its elements at about 1300°C. It rapidly absorbs moisture and carbon dioxide from air, producing sodium carbonate. $2NaOH + CO_2 = Na_2CO_3 + H_2O$. It is exceedingly soluble in water to which it imparts a strongly alkaline test and a soapy touch. The solution corrodes the skin, destroys vegetable tissues and has an *acrid taste* like that of soap or borax. It turns *red* litmus paper *blue*, and imparts a pink colouration to phenolphthalein. It liberates NH_3 from ammonium salts.

$$(NH_4)_2SO_4 + 2NaOH = Na_2SO_4 + 2NH_3 + 2H_2O$$

$$NH_4Cl + NaOH = NaCl + NH_3 + H_2O.$$

When NaOH sol. is added to the solution of a salt of a metal, the hydroxide of the metal is *usually* formed by double decomposition, and, if the hydroxide is *insoluble* in water, we get a precipitate.

$CuSO_4 + 2NaOH = Na_2SO_4 + Cu(OH)_2$ (*Pale-blue ppt.*) .

Sometimes the oxides of the metal are obtained.—

$Hg(NO_3)_2 + 2NaOH = H_2O + 2NaNO_3 + HgO$ (*yellew ppt.*)
$Hg_2(NO_3)_2 + 2NaOH = H_2O + 2NaNO_3 + Hg_2O$ (*grey ppt.*)
$2AgNO_3 + 2NaOH = 2NaNO_3 + H_2O + Ag_2O$ (*brown ppt*)

If the hydroxide [e.g., $Zn(OH)_2$, $Al(OH)_3$, $Sn(OH)_2$, $Pb(OH)_2$ etc.,] is amphoteric, the precipitate of the hydroxide which is first obtained dissolves when more NaOH solution is added to form a clear solution of the corresponding salt.

$$ZnSO_4 + 2NaOH = Zn(OH)_2 + Na_2SO_4$$
White ppt.

$$Zn(OH)_2 + 2NaOH = Na_2ZnO + 2H_2O.$$
Sod. zincate

$$Al_2(SO_4)_3 + 6NaOH = 2Al(OH)_3 + 3Na_2SO_4$$
White gelatinous ppt.

$$Al(OH)_3 + NaOH = NaAlO_2 + 2H_2O$$
Sod. aluminate.

Use.—Caustic soda is used in the manufacture of sodium, hard soap, paper and artificial silk, in bleaching and refining oils; in the purification of bauxite and in the laboratory as a reagent.

Sodium chloride, NaCl

Sodium chloride occurs in sea water to the extent of 2·6 per cent. As a mineral, it is found in *rock salt*.

In warm climates, common salt is obtained by the evaporation of sea water. Rock salt is obtained by direct mining generally, but sometimes water is sent down to the salt bed and the dissolved salt is pumped up and evaporated in pans.

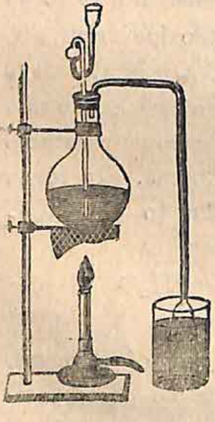


Fig. 99—Prep. of pure NCl.

Pure sodium chloride is obtained by passing HCl gas into a saturated solution of common salt in water. Pure sodium chloride is precipitated but the impurities remain in solution. The ppt. is filtered, washed with conc. HCl and then heated strongly in platinum crucibles to drive out HCl and water. (fig. 99).

Properties

Sodium chloride is a colourless, crystalline solid. It crystallises in the cubical form and it melts at 815°C. It is soluble in water. Its solubility increases, only slightly, with the rise of temp. Conc. H_2SO_4 decomposes it giving off HCl.

Use.—It is used as a necessary article of food; for preserving fish and meat; in salt-glazing earthenware articles, drain pipes, etc; for the extraction of sodium; and in the manufacture of sodium carbonate, HCl, caustic soda, chlorine, etc.

Sodium Carbonate, Na_2CO_3.—There are three different methods for the manufacture of sodium carbonate.

1. Leblanc process
2. The Ammonia-soda process or Solvay's process
3. The Electrolytic process

1. The Leblanc process.—Leblanc process is now obsolete. In this process, sodium carbonate used to be prepared by heating together sodium sulphate (salt cake), limestone and coke.

$$Na_2SO_4 + 4C = Na_2S + 4CO$$
$$Na_2S + CaCO_3 = Na_2CO_3 + CaS$$

2. The Ammonia-soda process (or Solvay's process).—This process which is also known as Solvay's process is by far the most important of the three processes.

Principle.—The process depends on the fact that when sod. chloride is treated with ammonium bicarbonate, NH_4HCO_3, sparingly soluble sodium bicarbonate is produced.

$$NaCl + NH_4HCO_3 = \downarrow NaHCO_3 + NH_4Cl$$

Sodium bicarbonate on ignition loses CO_2 to produce Na_2CO_3

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2$$

3. Details of the process—Cold brine is first of all saturated with ammonia gas in a tower fitted with shelves and overflow pipes during which the liquid is cooled by water (fig. 100). The ammoniacal brine thus produced is poured down another tower called Solvay's tower (fig. 101) from the bottom of which CO_2 gas is passed under a

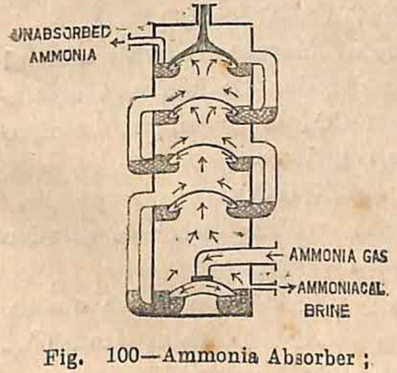


Fig. 100—Ammonia Absorber;

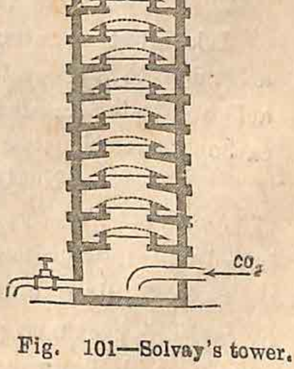


Fig. 101—Solvay's tower.

pressure of 1-2 atmosphere. Temperature is kept at about 30°—40°C. Sodium bicarbonate is produced by the following series of reactions.

$$NH_3 + H_2O + CO_2 = NH_4HCO_3$$

$$NaCl + NH_4HCO_3 = NaHCO_3 + NH_4Cl$$

The sodium bicarbonate crystals which separate are now filtered in vacuum filters, washed with a little water, dried and then strongly heated (calcined), when we get sodium carbonate, Na_2CO_3.

$$2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O.$$

Two by-products are obtained.

(1) CO_2 gas obtained, during calcination of sodium bicarbonate is used again.

(2) Ammonia is recovered for re-use from ammonium chloride by boiling it with lime.

3. **The electrolytic process.**—Sodium chloride is electrolysed in a diaphragm cell and the sodium metal which is liberated is converted into Na_2CO_3 by the joint action of steam and CO_2.

Properties.—Sodium carbonate is a transparent crystalline solid having the composition $Na_2CO_3, 10H_2O$. When exposed to the air, especially in dry weather, it effloresces—every one molecule of the **deca-hydrate** loses nine molecules of water of crystallisation and the substance falls to powder having the composition Na_2CO_3, H_2O, the **monohydrate.** When heated strongly, it first becomes **anhydrous** and then melts at 852°C but **does not** decompose. It is soluble in water, and the solution is alkaline to litmus and pehnolphthalein, due to **hydrolysis.**

$$Na_2CO_3 + 2H_2O \rightleftharpoons 2NaOH + CO_2 + H_2O.$$

Like all other carbonates, it produced effervescence with mineral acids due to the evolution of carbon dioxide. Sodium salt of the acid and water are also formed. When CO_2 is passed into sodium carbonate solution, sodium bicarbonate is produced .

$$Na_2CO_3 + H_2O + CO_2 = 2NaHCO_3.$$

As has already been pointed out, sodium carbonate solution boiled with milk of lime gives caustic soda.

Pure Sodium carbonate.—It is obtained in the laboratory by *carefully* heating a quantity of pure sodium bicarbonate to 250°—300°C in a platinum vessel *till the final weight is constant.*

Use.—It is used in the manufacture of soap and glass ; as a detergent (*i.e.*, for washing purpose) ; for removing permanent hardness in water; in the manufacture of caustic soda, other sodium compounds and aerated water; and in the laboratory as a reagent.

Sodium bicarbonate, $NaHCO_3$.—Acid carbonate of soda, as it is called, is obtained in the ammonia-soda process; it can also be prepared by passing CO_2 into sodium carbonate solution. It is largely used in medicine and in preparing *baking* powder.

Sodium nitrate (*Chili saltpetre*), **$NaNO_3$.**—Large quantities of sodium nitrate occur in the rainless districts of Chili, Bolivia and Peru. The salt is extracted out by treatment with water, and subsequently purified by fractional crystallisation.

Properties.—Sodium nitrate is a colourless, crystalline solid, very soluble in water. The crystals do not contain water of crystallisation. It is somewhat deliquescent, and, therefore, it cannot be used in the manufacture of gunpowder. When heated, it melts at 316°C and then decomposes with the rise of temperature giving off oxygen and yielding sodium *nitrite*. $2NaNO_3 = 2NaNO_2 + O_2$.

A piece of *glowing* charcoal or *feebly burning* sulphur thrown upon molten $NaNO_3$ takes fire and burns with great energy.

Sodium Sulphate (Glauber's Salt), Na_2SO_4, $10H_2O$.

Preparation.—Take dil. H_2SO_4 in a beaker and add Na_2CO_3 to it till there is no more effervescence. Filter the solution, and evaporate the filtrate to a small bulk and cool, when crystals of Glauber's salt separate out. $Na_2CO_3 + H_2SO_4 = Na_2SO_4 + CO_2 + H_2O$.

Properties.—Sodium sulphate is a colourless crystalline solid. It effloresces when exposed to the air. It is soluble in water. The solubility first rises with the rise of temperature up to a certain point and then it falls with the rise of temperature.

Use.—Sodium sulphate is used in medicine; in the manufacture of glass; the *anhydrous* salt is sometimes used as a dehydrating agent.

Detection of Sodium

As almost all compounds of sodium are *soluble* in water, we detect sodium by—

Dry Test.—Compounds of sodium on being heated on a piece of platinum wire, (rinsed with conc. HCl) in the non-luminous Bunsen flame, colour the flame, **golden-yellow,**

Exercise.

1. How is caustic soda prepared? State its properties. What change does it undergo on exposure to the atmosphere?

2. How is sodium carbonate commercially prepared? State its properties and uses. Is it produced in India?

3. How is *pure* sodium chloride prepared from common salt? Describe its properties and uses. Prove that Na_2SO_4 contains sulphur.

4. How is metallic sodium obtained from sodium hydroxide? State the properties and uses of the metal and the uses of two of its principal salts.

5. Describe the Solvay's process for the manufacture of sodium carbonate. How would you obtain caustic soda from it? Give outlines of the method with equations. *C. U. 1951 ; Cal. Pre. U., 1962.*

6. How is sodium carbonate manufactured by Solvay's Process? How would you obtain caustic soda from sodium carbonate? Give outlines of the methods with equations.

Explain with equations what happens when caustic soda solution is added to zinc sulphate solution gradually in excess. *Cal. Pre-U., 1961.*

7. How is caustic soda prepared from brine? What are its important uses? Explain with equation what happens when :

(*a*) Caustic Soda solution is added to zinc sulphate solution.

(*b*) Caustic Soda solution is added to copper sulphate solution. *Cal. Pre-U., 1962.*

8. Describe the preparation of Sodium Hydroxide. *Cal. Pre-U., 1964*

9. Give a short account of the Solvay Process for the manufacture of sodium carbonate. How would you prepare sodium hydroxide from sodium carbonate? *Cal. Pre-U. 1966.*

CHAPTER XXIII

POTASSIUM

Sumbol, K At. wt., 39·1 At. No. 19.

Occurrence.—The most important thing about potassium is its occurrence in soil as a vital element necessary for the growth of plants. As the potassium content of the soil is being used up by growing plants, it must be made up by supplying potassium-rich manures to the soil from time to time ; otherwise the soil will lose its fertility The chief world source of potassium is the famous Stassfurt deposit which contains minerals rich in potassium of which the most important are carnallite $KCl, MgCl_2, 6H_2O$, and kainite, $KCl, MgSO_4, 3H_2O$. Wood ash also contains about 30% potassium carbonate. Rocks such as granite contain potassium containing minerals *e.g.*, felspar, $K_2O, Al_2O_3, 6SiO_2$, the weathering of which gives rise to soil with its potassium content.

Extraction.—Potassium metal is not important, having very little use in industries At one time it used to be obtained by heating potassium carbonate strongly with charcoal.

$$K_2CO_3 + 2C = 2K + 3CO.$$

Now it is obtained like sodium by the electrolysis of fused caustic potash (Castner's process).

Properties

Physical.—It is a silver-white, soft metal. It is lighter than water having the sp. gr. of 0·86. It melts at 62°C to a liquid looking like mercury and boils at 757°C, forming a *green* vapour. In the *vaporous* state, its molecules are *monatomic*.

Chemical.—(1) *Action of air*—*Perfectly* dry air has no action. In ordinary air, freshly cut surface of the metal is rapidly covered with a film of the oxide which is gradually converted into the hydroxide and *then* into the carbonate. When heated in the air, potassium burns with a *violet* flame giving potassium oxides. (2) *Action of water*—The metal decomposes water at the ordinary temp. with much evolution of heat which ignites the hydrogen liberated. (3) When burning potassium is introduced into CO_2, potassium continues to burn in the gas forming K_2CO_3 and carbon is set free. $4K+3CO_2=2K_2CO_3+C$.

(4) When heated in CO, it forms potassium *carbonyl*.

(5) Heated in hydrogen at 300°C, it gives potassium hydride.

(6) *Action of halogens*—The metal burns spontaneously in contact with the halogens, with a violet flame, forming the halides. It forms an alloy with sodium and an amalgam with mercury.

Use.—There is no great demand for potassium in industry. An alloy of sodium and potassium is used in high-temp. thermometers.

Potassium-sodium alloy.—It is obtained by mixing the metals in the melted state. It is a liquid at the ordinary temp. looking like mercury.

Oxides of Potassium

There are two oxides of potassium.

Potassium monoxide, K_2O is obtained by heating potassium metal in a limited supply of air and **potassium peroxide** K_2O_4 in excess of air.

$$\underset{\text{pot. monoxide}}{4K+O_2=2K_2O} \quad \| \quad \underset{\text{pot. peroxide}}{2K+2O_2=K_2O_4}$$

Potassium monoxide and potassium peroxide are white and chrome yellow solids respectively. They react with water giving potassium hydroxide, but in the case of the pot. peroxide, oxygen is set free.

$$K_2O+H_2O=2KOH \ \| \ 2K_2O_4+2H_2O=4KOH+3O_2$$

Potassium hydroxide, caustic potash, KOH.—Caustic potash is prepared like caustic soda by the electrolysis of potassium chloride solution or by boiling pot. carbonate with milk of lime.

$$K_2CO_3 + Ca(OH)_2 = 2KOH + \downarrow CaCO_3$$

Properties.—Caustic potash is a white, crystalline solid. When heated, it melts at 360·5°C *without* decomposition and is frequently cast into sticks for convenience. It is extremely deliquescent, and absorbs moisture and CO_2 from the air producing a colourless liquid with a strong alkaline reaction. It is a stronger alkali than caustic soda. The aqueous solution of KOH sometimes known as *potash lye*, possesses an acrid taste and peculiar nauseous odour. It quickly destroys animal and vegetable substances. It cannot, therefore, be filtered except through glass-wool or sand. It neutralises acids.

Use.—It is used for absorbing CO_2 gas in preference to NaOH, for K_2CO_3 formed is more soluble in conc. KOH solution than Na_2CO_3 in conc. NaOH solution, on account of which if NaOH, is used for that purpose, Na_2CO_3 tends to separate out and interferes with the absorption of the gas. KOH is also used in the manufacture of soft soap.

Potassium chloride KCl.—It closely resembles rock-salt. It occurs in sea-water as well as in many mineral springs. It is the chief constituent of the salt-beds in Stassfurt, where it occurs as *sylvine*, KCl and carnallite KCl, $MgCl_2$, $6H_2O$.

Manufacture of KCl

(1) **From Carnallite.**—*By Fractional Crystallisation.*—Crude carnallite contains various impurities. It is crushed to powder and then treated with *mother-liquor*, left from previous operations, in large tanks into which steam is passed. Potassium chloride present in carnallite dissolves but not the other substances. After the impurities have settled down, the hot clear liquid from the top is run off and cooled, when potassium chloride crystallises out.

Properties.—It is a crystalline solid, soluble in water. It melts at 790°C.

Use.—It is used in the preparation of $KClO_3$, K_2CrO_4, KOH, K_2CO_3 ; in the manufacture of potash alum ; and for praparing artificial manures.

Potassium Bromide. KBr.—Preparation.—A mixture of bromine, **iron filings** and water is carefully heated in a flask fitted with a vertical condenser, till bromine is completely used up when Fe_3Br_8 is formed. On cooling, crystals of Fe_3Br_8 separate out. The sol. of Fe_3Br_8 is run into hot potassium carbonate solution until it is neutral, when iron hydroxides precipitate out. They are filtered off, and the filtrate is evaporated to crystallisation to get KBr.

$$\underset{[Fe_3Br_8]}{FeBr_2, 2FeBr_3} + 4K_2CO_3 + 4H_2O = 8KBr + 4CO_2 + Fe(OH)_2\ 2Fe(OH)_3$$

Properties.—It is a colourless crystalline solid. It is soluble in water and it melts at 750°C.

Use—It is used in medicine and in photography.

Potassium Iodide, KI.—Preparation—(i) It is prepared especially on a large scale, by the method adopted in the case of KBr. Iodine being used in place of bromine. (ii) It may be prepared by adding Iodine to KOH sol. till the solution is permanently yellow in colour. The sol. is evaporated when a mixture of KI and KIO_3 is left. The residue is mixed with carbon and the mixture is ignited till KIO_3 is completely decomposed. The mass is now cooled, treated with water, solution filtered and the filtrate is evaporated to crystallisation to get KI. $KIO_3 + 3C = KI + 3CO$

Properties.—It is a colourless, crystalline solid soluble in water. It melts at 705°C.

Use.—It is used in medicine; in photography; and as a reagent in the laboratory.

Potassium nitrate, KNO_3.—*Saltpetre* or *Nitre*, as it is called occurs as an efflorescent solid in Bengal and other hot countries.

Manufacture of KNO_3 From $NaNO_3$.—Potassium chloride is dissolved in *hot water* until the sp. gr. of the solution is 1·2 and sodium nitrate is added till the sp. gr. rises to 1·5. By *double decomposition*, KNO_3 and NaCl, are formed. NaCl, being the least soluble of the four salts, separates out from the hot solution. It is filtered off, and the hot filtrate is cooled, when KNO_3 crystallises out. KNO_3, thus. obtained, is purified by recrystallisation.

$$KCl + NaNO_3 = KNO_3 + NaCl.$$

Properties.—It is a *colourless*, *crystalline* solid, soluble in water. Unlike $NaNO_3$, it is *not* deliquescent. It is, therefore used in the manufacture of gunpowder. When heated, it first melts (336°C). and at a red heat decomposes into potassium nitrite and oxygen, $2KNO_3 = 2KNO_2 + O_2$. *Fused* KNO_3 is a powerful oxidising agent. Glowing charcoal, sulphur and phosphorus take fire in it and burn brilliantly. Preparation of **gunpowder** (KNO_3, 6 parts by wt., Charcoal 1 part; Sulphur 1 part) depends upon this fact.

$4KNO_3+5C=2K_2CO_3+3CO_2+2N_2$
$2KNO_3+2S=K_2SO_4+SO_2+N_2$
$4KNO_3+2S+6C=2K_2S+6CO_2+2N_2$

Use.—It is used in the laboratory : in medicine ; for the salting and pickling of meat to which it imparts a *red* colour ; in pyrotechny ; in the manufacture of gunpowder ; and as a fertiliser.

Potassium sulphate, K_2SO_4.—It may be prepared by treating potassium hydroxide or potassium carbonate with H_2SO_4.

Expt.—Take dil. H_2SO_4 in a beaker and to it add potassium carbonate till there is no further effervescence. Filter, and evaporate the filtrate to crystallisation, when potassium sulphate crystals separate out.

It may also be obtained by heating potassium chloride with conc. sulphuric acid.

Properties.—It is a crystalline solid and does not contain water of crystallisation. It is soluble in water.

Use.—It is used as as a purgative ; in the manufacture of potash alum and potassium carbonate. It is also used as a fertiliser.

Potassium carbonate, Pearl-ash, K_2CO_3—*Manufacture*—(i) **From Wood-ashes.**—Ashes of wood and other land plants contain potassium carbonate. Formerly, K_2CO_3 was extracted from these ashes by water and the sol. evaporated and calcined in pots, whence the name potash or *pot-ash.* For a long time this happensd to be the only source of the carbonate. Even now-a-days, in some parts of America, K_2CO_3 is obtained by that method. The wood is burnt in pits and the ashes are lixiviated with water in wooden tubs, sometimes with a little lime The clear liquid is drawn off and concentrated, when the less soluble impurities crystallise out. The mother-liquor is now evaporated to dryness and finally calcined. We get commercially pure K_2CO_3 called *pearl-ash.*

(ii) Pot. carbonate can also be prepared from KCl by means of Leblanc process.

N. B. Solvay's process is not available for the manufacture of K_2CO_3 because of the high solubility of $KHCO_3$.

Properties.—It is a white, crystalline, deliquescent solid. It is highly soluble in water, and the solution is alkaline to litmus, due to hydrolysis. A saturated solution of K_2CO_3 absorbs CO_2 producing **Potassium bicarbonate.**

Use.—It is largely used in the manufacture of soft soap, potassium ferrocyanide, potassium chromate, potassium bromide and iodide. It is also used in the manufacture of glass : and for preparing fusion mixture in the laboratory.

Fusion Mixture.—A mixture of K_2CO_3 and Na_2CO_3 in equivalent proportions is called *fusion mixture.* The mixture melts at a *lower* temp. than Na_2CO_3 and is used in chemical analysis.

Potassium permanganate, $KMnO_4$.—It is obtained by fusing KOH or K_2CO_3 with manganese dioxide and an oxidising agent like $KClO_3$ or KNO_3, when pot. manganate is obtained as a green mass. $3MnO_2 + 6KOH + KClO_3 = 3K_2MnO_4 + KCl + 3H_2O$.

The green mass is dissolved in water and then converted into pink pot. permanganate by adding dil. sulphuric acid or by passing carbon dioxide gas.

$$3K_2MnO_4 + 2H_2SO_4 = 2K_2SO_4 + 2KMnO_4 + MnO_2 + 2H_2O$$

$$3K_2MnO_4 + 2CO_2 = 2K_2CO_3 + 2KMnO_4 + MnO_2$$

The solution is decanted from the precipitated manganese dioxide. On concentration and cooling, deep purple red prisms of pot. permanganate are obtained.

Properties.—Potassium permanganate is a dark-purple crystalline solid. The crystals, when freshly prepared, possess a green metallic lustre, which, however, on exposure to the air, become of a steel-blue tint. It is isomorphous with potassium perchlorate. When heated, potassium permanganate decomposes into potassium manganate, manganese dioxide and oxygen.

$$2KMnO_4 = K_2MnO_4 + MnO_2 + O_2$$

At a red heat the manganate is also decomposed with evolution of oxygen. A mixture of $KMnO_4$ and phosphorus or sulphur takes fire when struck or rubbed, while a mixture of $KMnO_4$ and carbon takes fire only when heated, and not when struck. Permanganate of potash dissolves in water giving a solution of a very deep-purple colour. It attacks organic substances. Hence the solution cannot be filtered through filter-paper. *Glass-wool* is used for the purpose. It is a powerful oxidising agent ; can oxidise ferrous salt, oxalic acid, sugar, sulphurous acid, nitrous acid, etc.

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$$

$$5(H_2C_2O_2) + 2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 10CO + 8H_2O$$

Its value as an oxidising agent depends upon whether the sol. contains a free *alkali*, is *neutral*, or contains a free *acid*. Thus—

(1) *In alkaline*, or *neutral sol.*, 3 atoms of oxygen are available from 2 molecules of $KMnO_4$.

(*a*) $2KMnO_4 + 2KOH = 2K_2MnO_4 + H_2O + O$

(*b*) $\underline{2K_2MnO_4 + 2H_2O = 2MnO_2 + 4KOH + 2O}$

Adding, $2KMnO_4 + H_2O = 2MnO_2 + 2KOH + 3O$

(2) *In acidified sol.*, 5 *atoms* of oxygen are available from 2 molecules of $KMnO_4$. $2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$

Hence $KMnO_4$ acts as a more powerful oxidising agent in presence of an acid than in aqueous solution, or in presence of an alkali. With conc. H_2SO_4 potassium permanganate decomposes explosively, especially when heated.

Use.—It is used (i) in volumetric analysis ; and (ii) as a disinfectant.

Potassium dichromate, $K_2Cr_2O_7$; Preparation.—First of all sod. chromate is obtained by heating together chrome iron ore, soda ash and lime in an oxidising atmosphere in a rotatory furnace, lime serving to keep the mass porous.

$$\underset{\text{Chrome iron ore}}{4Fe(CrO_2)_2} + 8Na_2CO_3 + 7O_2 = 8Na_2CrO_4 + \downarrow 2Fe_2O_3 + 8CO_2$$

Sodium chromate is extracted from the mass by means of water. It is then treated with dilute sulphuric acid which changes it into sod. dichromate. $2Na_2CrO_4 + H_2SO_4 = Na_2Cr_2O_7 + Na_2SO_4 + H_2O$.

Now sod. dichromate is treated with pot. chloride when pot. dichromate being less soluble crystallises out.

$$2Na_2Cr_2O_7 + 2KCl = \downarrow K_2Cr_2O_7 + 2NaCl$$

Pot. dichromate forms large red tabular crystals. It dissolves in water to form an orange red solution. It is like pot. permanganate a powerful oxidising agent. In presence of dil. sulphuric acid, it oxidises sulphur dioxide into sulphuric acid, ferrous sulphate into ferric sulphate, liberates iodine from KI, itself being reduced to chromium sulphate, $Cr_2(SO_4)_3$, the solution turning green.

Use.—It is used (i) in electric cells ; (ii) as a reagent ; (iii) in the manufacture of other chromium compounds ; (iv) as an oxidising agent ; (v) in tanning industry ; and (vi) in dyeing industry.

Potassium Cyanide KCN.—It is prepared by fusing pot. ferrocyanide, $K_4Fe(CN)_6$ with metallic potassium.

$$K_4Fe(CN)_6 + 2K = 6KCN + Fe$$

It is deadly poisonous. It is used in the extraction of gold and silver, in electroplating and in analysis.

Exercise.

1. How does potassium occur in nature ? State its properties and uses.
2. State how the followings are prepared :
   KCl, $KClO_3$, $KMnO_4$ and $K_2Cr_2O_7$
3. What is pearl-ash ? How it is prepared ?

CHAPTER XXIV

COPPER AND ITS COMPOUNDS

Symbol Cu. At. wt. 63·5 At. No. 29

Occurrence.—Copper is found in the *free state* in nature near Lake Superior in America in the Ural mountains in Siberia and in Assam.

In the state of combination copper occurs :

(1) **as oxide**—*Ruby ore, Red copper ore* or *Cuprite*, Cu_2O.

(2) **as sulphide**—

Copper glance (*chalcocite*), Cu_2S ;

Copper pyrites (*chalcopyrite*), Cu_2S, Fe_2S_3 or $CuFeS_2$.

(3) **as carbonate**—Malachite, $CuCO_3$, $Cu(OH)_2$;

Azurite, $2CuCO_3$, $Cu(OH)_2$.

Extraction.—A large proportion of world's copper is extracted from copper pyrites, $CuFeS_2$. The extraction of copper is made difficult by the presence of a large proportion of iron and sulphur in the ore. It consists of the following operations :

1. **Concentration :** The ore if it is a low grade one is enriched by *oil floatation process*. The ore is crushed and finely ground. The ground ore is mixed with water, pine oil and other floatation reagents and then air is blown through the mixture. Particles of the ore rise up with the froth while the gangue matter collects at the bottom. The froth is skimmed off and allowed to settle. The concentrate, thus obtained, contains 25·35% of copper.

2. **Roasting :** The ore thus concentrated is now roasted with a view to convert by oxidation some of the iron into iron oxide and sulphur into sulphur dioxide, the latter escaping into the air or collected for the manufacture of sulphuric acid.

$$2CuFeS_2 + 4O_2 = Cu_2S + 2FeO + 3SO_2$$

3. **Smelting :** The roasted ore is now mixed with coke, silica and a little lime and heated in a reverberatory furnace when the iron oxide formed during roasting combines with silica to form a slag which is removed.

$$FeO + SiO_2 = \underset{\text{Ferrous silicate (slag)}}{FeSiO_3}$$

The residual ore called the **Matte** is a mixture of copper sulphide and iron sulphide containing about 50% of copper.

4. **Production of Blister Copper :** The matte is transferred while still molten into a Bessemer converter (for description, see manufacture of steel) lined with silica. Air is blown through the bottom of the converter. The remaining iron sulphide is oxidised into iron oxide and forms a slag with the silica lining. Copper sulphide now begins to oxidise and when two-third of it is converted into oxide, the latter reacts with the remaining unchanged sulphide to give **blister copper** which is so called because of blisters formed on the surface of the metal due to the escape of SO_2 during cooling.

$$2Cu_2S + 3O_2 = 2Cu_2O + 2SO_2$$
$$Cu_2S + 2Cu_2O = 6Cu + SO_2$$

5. **Refining of Blister Copper :** The impure blister copper is purified first (i) thermally and then (ii) electrolytically.

(i) *Thermal refining.*—The impure blister copper is melted on the bed of a reverberatory furnace and air is blown in. The impurities get oxidised and either escape as gases or form a slag with the silica lining of the furnace. Some copper too, may be oxidised into copper oxide. So anthracite coal is sprinkled on the surface and the molten mass is stirred with a green pole of wood to reduce any copper oxide formed back into copper.

(ii) *Electro-refining.*—For uses in electric industry, thermally refined copper is further purified by electrolysis. It is cast into blocks which are made the anodes in a bath of copper sulphate solution with thin sheets of pure copper suspended alternately from the cathode. On passing electric current, copper dissolves from the anodes and gets deposited on the cathodes of pure copper which therefore, grow thicker as the anodes grow thinner, the impurities falling to the bottom. (fig. 102).

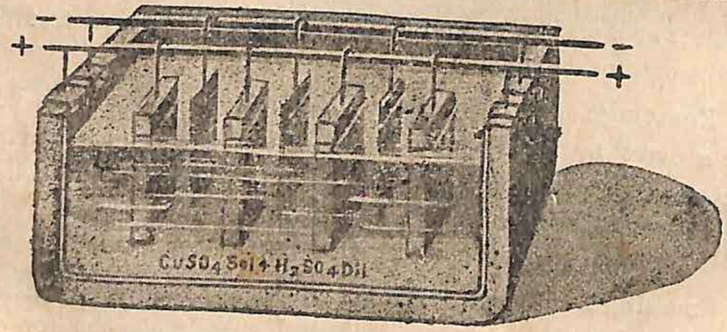


Fig. 102—Electro-refining of copper

Properties

Physical.—Copper possesses a peculiar red colour. It is soft, malleable and ductile, and has a sp. of 8 85. It is very tough. It melts at 1083°C. Just below its melting-point, copper becomes brittle. It is a good conductor of heat and electricity.

Chemical.—(1) *Action of air.*—Dry air has no action on the metal. When exposed to moist air it is covered with a brownish-grey film of oxide or sulphide ; and after a long time, with a green deposit of the basic sulphate. Heated in air, at the temp. of the oxy-hydrogen flame, it *burns* giving the oxide. (2) *Action of water.*—Pure copper is not attacked by water. (3) *Action of acids.*—Copper dissolves in HNO_3 producing cupric nitrate and usually the oxides of nitrogen. Dil. HCl has no action on copper and dil. H_2SO_4 has no action on it in absence of air. Conc. H_2SO_4 does not act upon the metal in cold ; but when heated, copper sulphate, SO_2 and water are formed. $Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O$. Hot conc. HCl *slowly* dissolves finely divided copper in presence of air. $2Cu + 4HCl + O_2 = 2CuCl_2 + 2H_2O$. When HCl gas is passed over heated copper, we get cuprous chloride and hydrogen.

Uses of Copper.—Copper largely used in electric industry : in electrotyping, electroplating ; in the preparation of household utensils, stills, etc. and in making alloys

Alloys of Copper.—The *alloys* of copper are made by adding different metals to molten copper in a reducing atmosphere. *Common brass*—alloys of Cu and Zn ; *Bronze* and *Copper coins* - alloys of Cu, Zn and Sn ; *Gun metal Bell* and *Speculum metal*—alloys of Cu and Sn ; *German silver*—alloys of Cu, Zn and Ni ; *Phosphor bronze*—alloys of Cu, Sn and P : *Aluminium bronze*—alloys of Cu and Al ; *Monel metal*—alloys of Cu and Ni ; *English silver coin*—alloys of Cu, Ag, Zn and Ni.

Oxides of Copper.

Cuprous oxide, Cu_2O—It is prepared by boiling alkaline $CuSO_4$ solution with grape sugar.

It is a red solid insoluble in water. When dissolved in conc. HCl, it gives cuprous chloride.

$$Cu_2O + 2HCl = Cu_2Cl_2 + H_2O.$$

It is used for imparting ruby red colour to glass.

Cupric oxide, CuO—It is prepared by heating copper in air, or the nitrate or the hydroxide or the carbonate of the metal. It is black in colour. It is reduced to the metal when heated with carbon, CO or H_2.

$$CuO + CO = Cu + CO_2$$

Use.—It is used in organic analysis, for imparting green tint to glass and as an oxidising agent.

Cuprous chloride, Cu_2Cl_2—It is prepared in the laboratory by boiling together cupric oxide, copper turnings, and concentrated HCl in a small flask and pouring the content into water when insoluble white ppt. of cuprous chloride is thrown down.

$$CuO + 2HCl = CuCl_2 + H_2O$$
$$CuCl_2 + Cu = Cu_2Cl_2$$

It is a white crystalline solid insoluble in water, but soluble in HCl and in ammonia. The solution in the latter is called ammoniacal cuprous chloride which absorbs oxygen, carbon monoxide and acetylene gas. It is used in gas analysis.

Cupric chloride, $CuCl_2$, $2H_2O$ (*green*) : **Preparation.**—It is obtained in the *anhydrous state* when copper is heated in chlorine. The *hydrated salt* is prepared by dissolving copper in *aqua regia* ; or its oxide, hydroxide, or carbonate in HCl. The solution on evaporation gives green crystals of $CuCl_2$, $2H_2O$.

Properties.—It is a green, crystalline solid, soluble in water. When heated, it first becomes anhydrous and, on further heating, decomposes into cuprous chloride and chlorine.

$$2CuCl_2 = Cu_2Cl_2 + Cl_2.$$

Cupric sulphate, $CuSO_4$, $5H_2O$ (*Blue vitriol—Tuntia*).

Preparation.—It may be prepared by heating copper with conc. H_2SO_4 or by heating CuO, $Cu(OH)_2$ or $CuCO_3$ with dil. H_2SO_4, and evaporating the solution to crystallisation.

Manufacture : *From Waste Copper.*—Waste copper is heated in a furnace and sulphur is thrown upon the red-hot metal, when copper sulphide is formed. Air is now admitted into the furnace whereby copper suiphide is converted into copper sulphate. The resultant mass is then cooled, treated with water, filtered and the clear filtrate is evaporated to crystallisation. We get crystals of *blue vitriol.*

$$Cu + S = CuS \parallel CuS + 2O_2 = CuSO_4.$$

Properties.—It is a blue, crystalline solid, containing *five* molecules of water of crystallisation. At 100°C it loses 4 molecules of water and is converted into a bluish-white salt having the composition $CuSO_4$, H_2O. At about 230°C it becomes *anhydrous* and *white* in colour. The anhydrous salt gets back its *blue* colour when treated with water. It is soluble in water.

Use.—Copper sulphate is used in electroplating, electrotyping and in some electric cells; in dying industry; as a germkiller and in medicine. Anhydrous copper sulphate is used for *detecting* small quantities of water in organic liquids.

Cupric nitrate $Cu(NO_3)_2, 3H_2O$

Preparation.—It may be prepared by dissolving copper, cupric hydroxide, CuO, or cupric carbonate in nitric acid. The sol., on being *carefully* evaporated, yields crystals having the composition $Cu(NO_3)_2, 3H_2O$.

Properties.—It is a blue, deliquescent, crystalline solid, containing three molecules of water of crystallisation. When heated strongly, it turns black, owing to decomposition into cupric oxide. It is highly soluble in water and in alcohol.

Carbonates of Copper.—Only basic carbonates of copper are known. They are all *cupric* compounds. Cuprous carbonates *do not exist*. The basic carbonates of copper precipitate out when the solution of a cupric salt is treated with alkali carbonates.

Detection of Copper

Dry test.—(1) Compounds of copper, when mixed with Na_2CO_3 and heated on charcoal under the *reducing blow-pipe flame*, are reduced to red scale of metallic copper. These red scales dissolve in conc. HNO_3 giving off brown fumes and producing a blue solution.

(2) Heated on a piece of Pt. wire moistened in conc. HCl, copper salts colour the *non-luminous* Bunsen flame *greenish-blue*.

(3) **Borax bead test.**—Heat a compound of copper on a borax bead in the oxidising flame of a Bunsen burner. The bead is coloured *blue*. Heat it in the reducing flame. The bead turns red and opaque.

Wet test.—(1) $NH_4(OH)$ added to the solution of a cupric salt, produces a *bluish-green* ppt. of the *basic* salt which dissolves in excess of $NH_4(OH)$ giving a deep blue sol.

$$2CuSO_4 + 2NH_4(OH) = (NH_4)_2SO_4 + Cu_2(OH)_2SO_4.$$

(2) H_2S passed into the acidulated solution of Copper salt gives a black ppt. of CuS which dissolves in conc. HNO_3 giving a *blue* solution.

(3) Potassium ferrocyanide solution added to the solution of soluble copper salt gives a chocolate ppt. of copper ferrocyanide. In *very* dilute solution only a colouration is produced.

(4) A piece of clean Iron, dripped into the solution of copper salt becomes coated with a red deposit of metallic copper.

Exercise.

1. Name the principal ores of copper. Describe any *one* process of extracting copper from its ores. Give equations. State the properties and uses of the metal.

2. Name two important alloys of copper with their constituents. Give their uses. How are copper oxides prepared ? *Punj., 1918 ; C. U., 1918, '41.*

3. Name the *oxides* and *chlorides* of copper, and state how you would prepare them. Describe their properties and indicate their uses. How is copper refined ?
Delhi, 1950 ; Mad., 1929 ; C. U., 1919 '22, '29, '34, '35, '37, '41.

4. What is *blue-vitriol* ? Give its preparation, properties, and uses. *C. U., 1919, '22, '24. '27, '36, '40.*

5. Starting with CuO, show how you will prepare—(*a*) $CuCl_2$, Cu_2Cl_2, (*b*) Blue vitriol.

6. State with equation what happens when metallic copper is heated with Conc. H_2SO_4. *Cal. Pre-U., 1964.*

CHAPTER XXV

SILVER

Symbol, Ag. At. wt., 108 At. No. 74

Silver is known from the earliest times. The alchemists called it Luna or Diana from the moon.

Occurrence.—Silver occurs free or native in large masses in Mexico, Norway and other places.

Extraction.—Besides native silver ore, the other two important ores of silver are Argentite. Ag_2S and chloroargyrite (Horn silver), AgCl. Several methods have been employed for the extraction of silver such as.

(1) The Amalgamation process.
(2) The Lead process.
(3) The Cyanide process.

1. The Mexican Amalgamation process.—In this process the crushed ore is mixed intimately with salt and other substances (magistral) as a result of which a silver amalgam is produced. Excess of mercury is then removed by distillation when silver is obtained. The process once largely used in Mexico is now almost obsolete.

2. The Lead Process.—When lead is extracted from argentiferrous lead ores such as galena, the lead obtained may contain silver up to 2 per cent. Lead also liberates silver from poor silver ores. Hence poor silver ores are smelted along with lead ores or with lead when we get also an alloy of lead and silver.

When the precentage of silver in Pb-Ag alloy is more than 1 per cent, silver can be recovered from lead by cupellation (See below). But if the precentage of silver in the alloy is less than 1 per cent, the alloy must be enriched in silver by processes which are known as *Desilverisation of lead.* Of the two processes of desilverisation (Pattinson and Parke). *Parke's procees* is more important which we describe below.

The Parke's Process —Theory.—It depends upon the fact that (i) when zinc is added to a melted alloy of silver and lead, zinc takes away silver from the alloy and itself forms an alloy with silver but *not* with lead ; (iii) the alloy of zinc and silver melts at a higher temperature than lead ; (ii) the alloy of zinc and silver is lighter than lead.

Details—The alloy of lead and silver is melted down in iron pots and the *requisite* quantity of zinc is added. The melted mass is thoroughly agitated and is then allowed to cool. The alloy of Zn and Ag is the first to solidify, and it rises on the surface. It is removed by perforated ladles. This alloy of Zn and Ag still contains lead. It is distilled, when zinc distils over and is removed. The enriched lead-silver alloy obtained as above is now cupelled in order to remove the remaining lead.

The Cupellation Process.—The alloy of Pb and Ag, rich in silver is taken in an oval-shaped dish, made of *bone-ash*, called the **cupel** *or* **test** (fig. 103A). The cupel is now placed on the bed of a reverberatory furnace, and a blast of air is projected on the alloy. Lead undergoes oxidation by the blast of air, but *not* silver. The melted oxide of lead (*Litharge*) is made to overflow by the force of the blast into iron pots below. After lead is thus completely oxidised and removed, and the thin film of *litharge*, still left, is absorbed by bone-ash, the bright surface of silver suddenly flashes out from below. This is known as the *flashing* of silver. The metal is then removed.

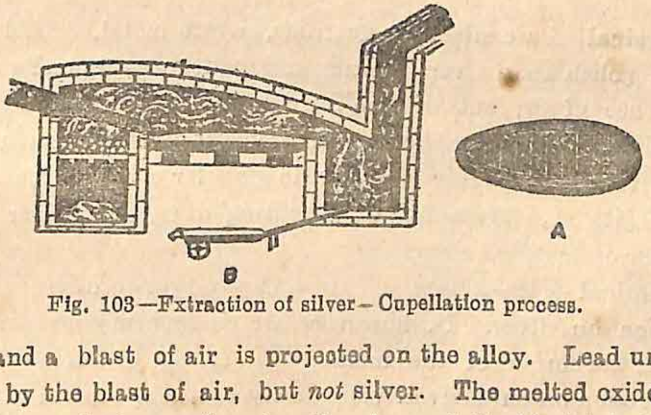


Fig. 103—Fxtraction of silver—Cupellation process.

3. The Cyanide Process.—The finely crushed ore of silver is treated with a dilute solution (0·7%) of sodium cyanide in water, and a current of air is passed through the solution. Sodium cyanide reacts with silver sulphide giving soluble sodium argento-cyanide.

The silver is now precipitated from the filtered sol. by the addition of scrap zinc or aluminium dust. The precipitated silver is filtered, washed and purified.

$$Ag_2S + 4NaCN \rightleftharpoons 2NaAg(CN)_2 + Na_2S$$
$$2NaAg(CN)_2 + Zn = 2Ag + 2NaCN + Zn(CN)_2$$

N. B.—The reaction between Ag_2S and NaCN is reversible. The result is that Na_2S fromed, starts the *reverse* action. A stream of air is passed into the solution to oxidise the Na_2S into Na_2SO_3, Na_2SO_4, and sulphur, so that reverse action is prevented.

Electro-refining of Silver.—A solution of *pure* $AgNO_3$ in water is taken in a vessel and treated with 1%HNO_3. A plate of pure silver dipping in the liquid is made the cathode, while the sample of the impure metal (say a *silver coin*), to be refined, is suspended from the anode. Electric current is passed, when pure silver is deposited on the cathode, while silver from the impure samples goes into solution. The impurities present like copper, gold, etc. either dissolve or are deposited at the bottom.

Properties

Physical—Pure silver is a lustrous, white metal, capable of taking a high polish and is very ductile and malleable. It melts at 960·5°C in absence of air, but at 955°C in air. The molten metal absorbs about 22 times its volume of oxygen which it gives up during solidification driving out some fused silver in globular masses. This is known as the 'spitting', 'vegetation', or 'sprouting' of silver. Silver *is the best conductor of heat and electricity*.

Chemical—(1)—*Action of air.*—Dry air or ordinary air has got no action on silver. If, however, air be contaminated with H_2S, it blackens the surface of the metal. (2) *Action of water.*—Pure water has no action on pure silver. (3) *Action of acids.*—Silver is practically unattacked by HCl. Nitric acid, hot or cold, dil. or conc., readily dissolves the metal forming silver nitrate. Dil. H_2SO_4 has no perceptible action on silver. Hot and conc. H_2SO_4 dissolves silver giving off SO_2 and producing Ag_2SO_4. (4) *Alkalis* have no action on silver. (5) The metal is attacked by H_2S producing a black stain on the surface of the metal. The stain may be easily removed by potassium cyanide.

Use.—It is used in preparing alloys and ornaments ; in coinage ; in the preparation of chemical utensils (for it is not attacked by fused alkalis); in preparing $AgNO_3$; in silver voltameter: and in electroplating.

N. B.—As pure silver is too soft for ordinary uses it is alloyed with metals like copper, etc. to make it hard: and the alloy is used for preparing coins and ornaments.

Fineness of Silver.—The purity of silver is expressed by the amount of silver that an alloy cantains in 1000 parts of it. This is known as the *fineness* of silver. Thus *pure* silver is 1000 *fine*. *English Standard silver* is 925 *fine*, meaning thereby that 1000 parts of the alloy contain 925 parts of silver and 75 parts of copper or of other metals. Lumps of silver, used in commerce, are alled 'bullion'.

Silver Monoxide, Ag_2O is obtained as a brown ppt. by adding caustic soda solution to silver nitrate solution.

$$2AgNO_3 + 2NaOH = \downarrow Ag_2O + 2NaNO_3 + H_2O$$

It is a greyish black powder. When heated to above 250°C, it breaks up into silver and oxygen. $2Ag_2O = 4Ag + O_2$. It is an oxidising agent.

Silver chloride, AgCl.—It occurs as *Horn silver*. It is readily prepared as a curdy white ppt. by adding HCl, or a soluble chloride, to silver nitrate solution. $AgNO_3 + HCl = AgCl + HNO_3$.

Properties.—It is a white solid which melts to a dark-yellow liquid at 460°C. It is insoluble in water, but dissolves readily in ammonia, sodium thiosulphate and potassium cyanide solutions.

$$AgCl + 2KCN = KAg(CN)_2 + KCl.$$

When exposed to light, it first becomes *violet*, then *grey* and ultimately *black*.

Silver nitrate.—(*Lunar caustic*), $AgNO_3$.—This is the most important salt of silver. It is obtained by dissolving silver in excess of warm, *moderately* dil. HNO_3, and evaporating the acidic liquid to crystallisation. $Ag + 2HNO_3 = AgNO_3 + NO_2 + H_2O$.

When prepared from sterling silver (or *silver coin*), the solution will contain both $AgNO_3$ and $Cu(NO_3)_2$. Silver nitrate may be separated from $Cu(NO_3)_2$ thus :—

Evaporate the mixture of $AgNO_3$ and $Cu(NO_3)_2$ sols., when crystals of $AgNO_3$ mixed with those of $Cu(NO_3)_2$ are obtained. Now heat the crystals to 250°C, when $Cu(NO_3)_2$ decomposes into CuO, N_2O_4 and O_2 but not $AgNO_3$. Cool the residue, treat it with water and filter. Evaporate the filtrate to crystallisation. We get crystals of $AgNO_3$.

Properties.—It is a colourless, crystalline solid, soluble in water. When heated to 209°C it melts, and the fused mass is cast into sticks and used under the name of *lunar caustic*. It decomposes at 450°C;

giving silver nitrite. $2AgNO_3 = 2AgNO_2 + O_2$. Heated still further, $AgNO_2$ decomposes giving metallic silver. $2AgNO_2 = 2Ag + 2NO + O_2$. It possesses powerful corrosive action on organic tissues, which it turns black especially in presence of light. The blackening is due to finely divided metallic silver reduced from the nitrate by the organic matter. Dry silver nitrate absorbs ammonia forming $AgNO_3, 3NH_3$. A solution of silver nitrate also blackens when exposed to light in contact with organic substances. Hence $AgNO_3$ solution mixed with gum-water, is used for the preparation of *marking-inks*. Silver nitrate should be kept in blue or amber-coloured bottles. $AgNO_3$ is soluble in alcohol.

Use.—It is used in photography ; in medicine ; in volumetric analysis ; for silvering mirrors ; and for preparing marking-inks.

Silver Sulphate, Ag_2SO_4.—It is formed when silver is boiled with conc. H_2SO_4 ; or when $AgNO_3$ solution is treated with H_2SO_4 or a soluble sulphate. $2AgNO_3 + K_2SO_4 = Ag_2SO_4 + 2KNO_3$.

Properties.—It is a crystalline solid, sparingly soluble in water. It dissolves in dil. HNO_3. Silver sulphate begins to decompose at 917°C and is completely redneed at 923°C. $Ag_2SO_4 = 2Ag + SO_2 + O_2$.

Silvering and Silver plating.—Articles of Brass, Bronze, Copper, etc. are given a silver-like appearance by providing them with a coating of silver. When the coating is rather thick, it is called 'silver-plating' ; when the coating is thin, it is called 'silvering'. The following methods are employed :—

Electroplating.—Take a solution of a double cyanide of silver and potassium in a vessel and introduce two electrodes into it from an electric cell. Suspend the *cleansed* articles, to be silver-plated from the cathode and a plate of pure silver from the anode. Pass electric current through the solution, when the articles will be silver-plated (fig. 104).

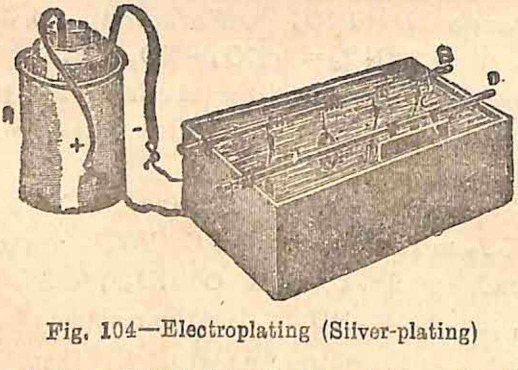


Fig. 104—Electroplating (Silver-plating)

Detection of Silver

Dry test.—Compounds of silver mixed with Na_2CO_3 and heated on charcoal in the reducing blow-pipe flame yield a brilliant button of silver.

Wet test,—(1) To the sol. of silver salt add dil. HCl. when a *white* ppt. of AgCl, insol. in conc. HNO_3 but readily soluble in NH_4OH, is obtained. The ppt. (*viz* AgCl) also turns violet on exposure to light.

(2) To the sol. of silver salt add K_2CrO_4 sol. when a *red* ppt. of Ag_2CrO_4, soluble in HNO_3 is produced.

(3) To the sol. of silver salt add Cu or Zn, when a ppt. of Ag is obtained. Ag is also partly deposited on Cu or Zn.

Photography.—It depends upon the action of light on silver halides. Some chemical change of unknown nature, (incipient reduction) takes place when silver halides are exposed to light. If after exposure to light the silver halide is subjected to the action of a reducing agent, it is further reduced to black particles of silver.

A photographic plate (or film) is coated with a uniform deposit of silver bromide dispersed evenly in gelatine. Light from an object to be photographed (Man, landscape etc.) is brought to a focus on the plate by means of the lens of a camera for a few seconds. The plate is *developed* by immersing it in a solution of an organic reducing agent (e.g., hydroquinone). The part affected by light is reduced to black particles of silver, the rest of the AgBr remaining unchanged. Now the unchanged AgBr is dissolved out in a *fixing bath* made of sodium thiosulphate $Na_2S_2O_3$ $5H_2O$ (Photographer's hypo). We have now got what is known as photographer's *negative*, which is so called because the brighter parts of the object appears darker and the darker parts lighter in it. From the negative, the ordinary photograph (called the *positive*) is obtained by laying the negative on a *print paper* which like photographic plate is coated with a layer of AgBr. The combination is now exposed so that light passes through the negative before it reaches the print paper. The print paper is then developed and fixed in the same manner as has been done in producing the negative.

Exercise

1. How does silver occur in nature ? What are the processes of desilvering lead ? Give the properties and uses of the metal.

2. What is *lunar caustic* ? Give its preparation, properties and uses. *Banaras, 1935; Nag., 1930.*

3. What do you mean by (*a*) flashing of silver. (*b*) fineness of silver, (*c*) spitting of silver ? What is the action of ammonium hydroxide and KCN solution on AgCl ? *Bom., 1930 : Banaras. 1933; Punj. 1921; C. U.. 1941.*

4. How is silver-plating carried out electrolytically ?

5. Describe the principal method by which silver, is extracted from its ores and mention the principal uses of the metal and its important compounds.

6. Write a short note on the chemistry of photography. *Punj., 1927,' 32,' 35.*

7. Write a short note on cupellation.

CHAPTER XXVI

CALCIUM

Symbol, Ca At. wt., 40 At. No., 20

Occurrence.—Calcium does not occur free in nature but its compounds are widely distributed. It occurs—

(1) **as Carbonate,** in the form of *Limestone, Chalk, Marble, Coral, Calcite, Calcspar, Icelandspar*, $CaCO_3$.

(2) **as Sulphate,** in the form of *Gypsum*, $CaSO_4, 2H_2O$, and *Anhydrite*, $CaSO_4$.

(3) **as Fluoride,** in the form of *Fluorspar*, CaF_2; and

(4) **as Phosphate,** in the minerals *Apatite*, and *Phosphorite* $Ca_3(PO_4)_2$, etc.

Shells of eggs, oysters, pearls, cuttle-fish etc. are mainly composed of calcium carbonate ; white bones of animals are made of calcium phosphate.

Extraction of Calcium.—Calcium is obtained by the electrolysis of fused calcium chloride whose melting point has been lowered by the addition of a small quantity of fluorspar. The electrolysis is carried out in a graphite cell with graphite anodes and a water cooled iron rod acting as a cathode. The iron cathode just touches the surface of the molten bath (700°C) at the begining. On electrolysis, calcium metal liberated at the iron cathode sticks to the latter. The iron cathode is gradually raised so that a rod of calcium is formed below it and now functions as a cathode instead of the iron rod. When the rod of calcium has grown sufficiently long, it is removed. Chlorine sets free at the anode is led away through flues. (fig. 105).

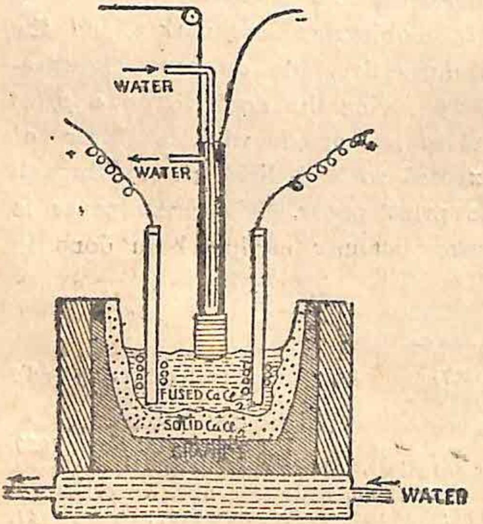


Fig. 105—Extraction of calcium

$$Ca^{++}Cl_2^{--} \rightleftharpoons Ca^{++} + 2Cl^-$$

$$\begin{array}{lcl} Ca^{++} + 2e & = & Ca \\ 2Cl^- & = & Cl_2 + 2e \\ \hline Ca^{++}Cl_2^{--} & = & Ca + Cl_2 \end{array}$$

Properties : Physical.—It is a *soft*, *malleable*, silver-white metal. Its sp. gr. is 1·52, and it melts at about 800°C.

Chemical.—(1) *Action of air.*—Calcium can retain its lustre in dry air, but tarnishes when exposed to moist air due to the formation of the oxide. When heated in air it burns producing CaO with a *little* Ca_3N_2. (2) *Action of water*—It decomposes, water at the ordinary temp. like sodium and potassium, liberating hydrogen; but less energetically than either of them, $Ca + 2H_2O = Ca(OH)_2 + H_2$. (3) *Action of acids.*—With acids (excepting HNO_3) calcium gives H_2 and calcium salts of the acids. (4) When heated in Cl_2, it gives calcium chloride. (5) Heated in hydrogen, calcium forms calcium hydride, CaH_2; and (6) heated to *dull-red* heat in nitrogen, calcium gives calcium nitride, Ca_3N_2.

Use.—Calcium metal is used to remove last traces of water from absolute aclohol. It is also used for the preparation of calcium hydride and for separating argon from nitrogen.

Oxides of Calcium.—Calcium forms many oxides, of which the monoxide, CaO commonly known as *quicklime* is more important.

Manufacture of quick lime—Quick lime is obtained by heating limestone to a temperature of 800°C—1000°C in kilns. $CaCO_3 = CaO + CO_2$. On a small scale, an intermittent type of kilns are used (fig. 106) whereas on a large scale, continuous type of kilns are used.

In an intermittent Kiln, fire is made below an arch made of limestones. CO_2 gas is swept away in the draught set up by the fire. The whole process takes about 26—48 hrs. After that period, the kiln is broken and the lime is removed.

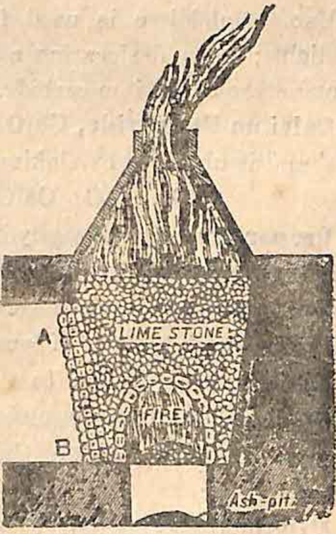


Fig. 106—Manufacture of quick lime—Intermittent process

In the continuous Kiln, limestone is fed through a hopper at the top of the furnace and lime is raked out continuously through a side hole near the bottom. Producer gas generated from coke is burnt in a fire place constructed by the side of the furnace, the hot gases and the flame playing upon and passing through the pile of lime stones. The process is continuous and the lime obtained is not mixed with the ash of the furnace.

Properties.—Quicklime is a white amorphous solid. It does not melt but becomes incandescent even when heated in oxy-hydrogen flame. It can, however, be melted in the electric furnace (m.p. 2570°C). It vigorously combines with water with a hissing sound producing much heat. $CaO + H_2O = Ca(OH)_2$ (slaked lime).

When left to the atmosphere, it slowly combines with the moisture and CO_2 of the air, being converted into calcium hydroxide and calcium carbonate respectively.

At the temperature of the electric furnace, quicklime reacts with coke to produce calcium carbide. $CaO + 3C = \underset{\text{cal. carbide}}{CaC_2} + CO$.

It dissolves in an acid to form calcium salt of the acid and water. It disengages ammonia from ammonium salts.

Use.—Quicklime is used for preparing slaked lime ; for producing limelight ; as a desiccating agent ; as a 'flux' in metallurgy : in the manufacture of calcium carbide.

Calcium Hydroxide, $Ca(OH)_2$,—It is commonly known as '*slaked lime*' and is obtained by slaking quicklime with water.

$$CaO + H_2O = Ca(OH)_2$$

Properties.—Calcium hydroxide is a *white* ; *amorphous* powder, When strongly heated (at 450°C), nearly all the water is driven off and we get calcium oxide. It is *sparingly soluble* in water ; its solubility *falls* with the rise of temperature.

Lime-water.—When to a little slaked lime a large excess of water is added, slaked lime dissolves in water giving a clear solution called **lime-water**. Lime-water, therefore, is a solution of calcium hydroxide in water.

Milk-of-lime.—When to a small quantity of water an excess of slaked lime is added, with stirring, a portion of the slaked lime dissolves in water giving a *saturated* solution of lime in water, but the remaining portion is held in suspension. In short, we get an emulsion, as it were of lime and water. It appears milk-like, and is called **milk-of-lime.**

The solution of calcium hydroxide in water has alkaline reaction (turns *red* litmus-paper *blue*) and absorbs carbon dioxide producing calcium carbonate, $Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$.

Use.—Slaked lime is used in the preparation of mortars and cements ; in the manufacture of glass, bleaching powder, caustic soda ; for purifying gases ; in tanning industry ; as a disinfectant, as a fertiliser ; also for disengaging ammonia from ammonium salts.

Mortars and Cement.—Common mortar (or *lime-mortar*) is made by mixing slaked lime with three or four times its bulk of sand or brick-dust and making the whole into paste with water. When the water evaporates, a porous material remains. This now gradually absorbs CO_2 from the air and the lime passes into calcium carbonate. The crystalline calcium carbonate formed adheres to and is interlaced with the sand or brick-dust giving a rigid but porous mass which sticks firmly to the brick or stone. The mortar is then said to set. **The setting of mortar** is due to two causes : (i) loss of water on account of evaporation ; and (ii) absorption of CO_2 from the air and the gradual conversion of lime into calcium carbonate, $CaCO_3$.

If no sand or brick-dust were used in the preparation of mortars, then the mass would not be able to bind the bricks firmly. The lime after the evaporation of water would occupy a smaller space than before and cracks would be formed due to shrinkage. **Sand serves two purposes** :—(i) It prevents shrinkage of the mortar in the course of drying ; and (ii) makes the mass porous so that the atmospheric CO_2 may freely penetrate inside the mass, thus facilitating the setting of mortar.

Cement mortar is a paste made with cement, sand and water.

Cement.—It is prepared by *burning* a mixture of limestone and clay. The *clinker*, as the resultant mass is called, is powdered and sieved and we get the greyish, powder-like substance. Cement differs from *ordinary lime* in the fact that it *sets under water*.

Calcium Chloride, $CaCl_2, 6H_2O$.—It may be prepared by dissolving lime or calcium carbonate in hydrochloric acid and evaporating the solution to crystallisation.

$$CaCO_3 + 2HCl = CaCl_2 + CO_2 + H_2O.$$

Properties.—Calcium Chloride is a colourless, crystalline, deliquescent solid. On strong heating, it becomes anhydrous. The anhydrous calcium chloride readily absorbs moisture and ammonia gas. Hence it is used as a drying agent, though it cannot be used for drying ammonia gas.

Use.—As a drying agent, in freezing mixture and also in medicine.

Calcium sulphate.—Occurrence.—It is met with in nature as the hydrated compound *gypsum*, $CaSO_4$, $2H_2O$ and in the anhydrous form as *anhydrite*, $CaSO_4$ (*Alabaster* is highly crystalline gypsum, while *selenite* is another variety of calcium sulphate.)

Preparation.—Calcium sulphate may be prepared in the laboratory by the action of dilute sulphuric acid on lime, powdered chalk, marble, etc. or by double decomposition. Precipitated gypsum is formed by adding H_2SO_4 to $CaCl_2$ solution.

Properties.—It is *white, crystalline solid* slightly soluble in water. The solubility at first *rises* and then *falls* with the rise of temp. When gypsum is heated to about 120°C, it loses a portion of its water of crystallisation and is converted into Plaster of Paris. At 200°C it becomes anhydrous.

Plaster of Paris., $(CaSO_4)_2$, H_2O—partially dehydrated Gypsum.

Manufacture.—Plaster of Paris is manufactured by *burning* gypsum in a kiln or oven in such a way that—(i) the temp. is not allowed to rise above 120°C, for above this temp. it becomes *deadburnt* and does not set with water ; and (ii) gypsum does not come into contact with carbonaceous fuel, for in that case it will be reduced partly into the sulphide. $2(CaSO_4, 2H_2O)=(CaSO_4)_2, H_2O+3H_2O$.

Properties.—Plaster of Paris is a *white powder* which forms a hard mass with water. This is known as *setting* of Plaster of Paris. It is due to *re-hydration* and re-conversion into gypsum.

$$(CaSO_4)_2, H_2O+3H_2O=2(CaSO_4, 2H_2O).$$

Uses of Calcium sulphate.—Gypsum is used for manufacturing Plaster of Paris ; as a fertiliser ; for filiing or glazing paper ; and forms the chief component of *crayons* (or chalk pencils). Plaster of Paris is used for making *moulds* in pottery work and other purposes ; in surgical bandages ; as a cement in ornamental casting ; and in preparing busts, statues, etc.

Calcium nitrate.—It may be prepared by treating lime, marble or chalk with dil. nitric acid.

Preparation in the Laboratory.—Take dil. HNO_3 in a beaker and add $CaCO_3$ to it till there is no more effervescence. Filter the solution and evaporate the filtrate to crystallisation.

Properties.—It is a *crystalline, deliquescent* solid, highly soluble in water. When heated, it decomposes into lime, N_2O_4 and O_2.

$$2Ca(NO_3)_2=2CaO+2N_2O_4+O_2.$$

Use.—It is used as a fertiliser.

Calcium Carbonate.—It occurs in nature as huge deposits of marble, lime stone, chalk etc. It may be obtained as a white precipitate by the action of sodium, potassium or ammonium carbonate solution on the solution of a calcium salt. It may be prepared by the action of CO_2 on lime. Obtained in the wet way, it is called *precipitated chalk*.

Properties.—It is a tasteless, white solid insoluble in water, but it readily dissolves in water containing CO_2 due to the formation of $Ca(HCO_3)_2$. Like all other carbonates, it reacts with acids with effervescence. When heated, it breaks up giving CaO and CO_2.

Calcium Carbide.—It is manufactured by heating a mixture of lime and carbon in an electric furnace. $CaO + 3C = CaC_2 + CO$.

Properties.—It is a hard, brittle crystalline solid possessing a bronze colour due to the presence of impurities. The pure substance is white in colour. Calcium carbide reacts with water giving off acetylene. When heated to about 1200°C in a current of nitrogen, it forms calcium cyanamide. $CaC_2 + N_2 = CaCN_2 + C$.

Use.—Calcium carbide is used for the preparation of acetylene and calcium cyanamide. The latter substance is used as an artificial feritiliser.

Superphosphate of lime, $CaH_4(PO_4)_2$.

Tricalcium phosphate (bone ash or rock phosphate), $Ca_3(PO_4)_2$ being insoluble in water is not of much use as a fertiliser. But it can be converted into soluble form by heating it with chamber acid in a brick chamber for 2-3 days. By this treatment tricalcium phosphate is changed into monocalcium tetrahydrogen diphosphate, $CaH_4(PO_4)_2$ which is otherwise known as superphosphate of lime.

$$Ca_3(PO_4)_2 + 2H_2SO_4 = 2CaSO_4 + CaH_4(PO_4)_2$$

Being soluble in water, plants can utilise it when used as a fertiliser.

Detection of Calcium

Dry test.—*Flame test*—Compounds of calcium when heated on platinum wire moistened with conc. HCl in the non-luminous Bunsen flame, impart a transient, *brick-red* colour to the flame.

Wet test.—(i) Ammonium carbonate sol. added to the solution of a calcium salt gives a white precipitate of calcium carbonate.

$$CaCl_2 + (NH_4)_2CO_3 = CaCO_3 + 2NH_4Cl.$$

(ii) Ammonium oxalate solution added to the solution of a calcium salt, gives a *white* precipitate of calcium oxalate, *insoluble* in acetic acid.

$$CaCl_2 + (NH_4)_2C_2O_4 = CaC_2O_4 + 2NH_4Cl.$$

Exercise

1. How is marble converted into quicklime? Describe the effect of adding (*a*) HCl and (*b*) water to each of these substances and state the conclusions to which these experiments lead. *Cam. Jun,, C.U., 1910, '45.*

2. Distinguish between *quicklime* and *slaked lime*. How are they prepared on a large scale and what are their principal uses? How would you prepare a sample of pure anhydrous calcium chirride from them? What are the principal uses of fused calcium chloride in the laboratory? How will you prepare—(*a*) *slaked lime*, (*b*) *lime-water and* (*c*) *milk-of-lime* from quicklime.

C. U., 1917, 19, '21, '22, '24, 26, '27, 29, '45,

3. Describe how you would prepare (*a*) Plaster of Paris and (*b*) Lime. Give outlines of the methods with equations. Describe also the uses of these compounds. *Cal. Pre-U., 1964, '67.*

4. Describe briefly the preparation of Quicklime. Give equations. *Cal., Pre-U., 1965.*

CHAPTER XXVI

MAGNESIUM

Symbol, Mg At. wt., 24 At. No.. 12

Magnesium belongs to Gr. IIB of the periodic table.

Occurrence

(1) as Carbonate

Magnesite, $MgCO_3$

Dolomite, $CaCO_3$, $MgCO_3$.

(2) as Sulphate

Kieserite, $MgSO_4$, H_2O.

(3) as Chloride

Carnallite, $MgCl_2$, KCl, $6H_2O$.

Extraction.—The metal magnesium is obtained by the electrolysis of fused carnallite, KCl, $MgCl_2$, $6H_2O$.

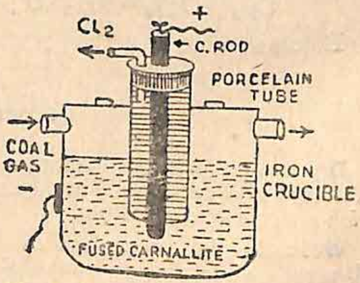


Fig. 107—Extraction of magnesium from fused carnallite.

(1) **Details.**—Either carnallite or a mixture of anhydrous $MgCl_2$ and NaCl, in *right proportion* is taken in a covered *iron* crucible and is strongly heated, when carnallite loses water. The mass fuses to a clear liquid. The crucible is made the *cathode* by being connected with the *negative* pole of a battery: while the *anode*, connected with the *positive* pole of the same battery, consists of a stout carbon rod which dips into the fused material. The carbon rod

is placed inside a porcelain cylinder, provided with an exit tube, for the escape of chlorine. Air from inside the crucible is replaced by coal-gas. On now passing electric current, $MgCl_2$ *alone* undergoes decomposition. Magnesium is liberated at the *cathode*, and Cl_2 liberated at the *anode* is removed (fig. 107). The metal is taken off and is purified by distillation.

$$MgCl_2 = Mg + Cl_2.$$

Properties : Physical.—Magnesium is a silver-white, malleable and ductile metal. Its sp. gr. is 1·74. It melts at 659°C and boils at 1120°C.

Chemical—(1) *Action of air.*—Dry air does not affect its silver-white lustre, but in moist air, a coating of MgO is formed. Heated in air, it burns with a dazzling white light rich in actinic rays producing MgO and a *little* Mg_3N_2. It burns in oxygen giving MgO.

(2) *Action of water.*—Heated magnesium burns in steam, and decomposes boiling water. $Mg + H_2O = MgO + H_2$. (3) *Action of acids.*—It dissolves in dilute acids giving off hydrogen. (4) *Action of alkalis.*—Alkalis have no action on magnesium. (5) It combines with nitrogen, when strongly heated in the gas forming magnesium nitride, Mg_3N_2. $3Mg + N_2 = Mg_3N_2$. (6) Burning magnesium continues to burn in carbon dioxide liberating carbon and forming magnesium oxide, $2Mg + CO_2 = 2MgO + C$. At a very high temp. magnesium acts as a *powerful reducing* agent.

Use.—*Magnesium* is used in photography ; for signalling ; in fire works ; and in the preparation of some *light* alloys like *electron* (alloy of Mg and Zn), *magnalium* (alloy of Mg and Al), etc.

Magnesium oxide (Magnesium), MgO.—It is usually obtained by heating either the *basic carbonate of magnesium* or *magnesite.*

Properties.—It is a *white* powder, which can stand a very high temp. It fuses at the temp. of the oxy-hydrogen blow-pipe flame (*Cf. lime*). When heated with carbon in the electric furnace, it gives magnesium carbide. It very slowly reacts with water, especially when the latter is boiling, producing $Mg(OH)_2$; and when moist, it turns *red* litmus-paper *blue.* Exposed to most air, it absorbs CO_2 producing magnesium carbonate.

Use.—It is used in the manufacture of *refractory bricks* (firebricks) and crucibles ; for lining electric furnaces ; as a *lagging* for steam pipes ; as an absorbent ; and in medicine.

Magnesium hydroxide, $Mg(OH)_2$.—It is obtained as a white ppt. when caustic soda or caustic potash solution is added to the solution of a soluble salt of magnesium.

$$MgSO_4 + 2NaOH = \downarrow Mg(OH)_2 + Na_2SO_4.$$

It is a white powder, only slightly soluble in water, to which it imparts an alkaline reaction. It is soluble in ammonium chloride.

Magnesium Chloride, $MgCl_2$, $6H_2O$.—In the hydrated form, it is prepared by the general method of preparing a soluble salt, i.e., by dissolving either the metal or its oxide or the carbonate in dilute hydrochloric acid. The solution is concentrated and cooled when crystals having the composition $MgCl_2, 6H_2O$ are obtained.

Anhydrous magnesium chloride cannot be prepared by heating the hydrated salt, because such an attempt will lead to its decomposition with elimination of hydrochloric acid,

$$MgCl_2, 6H_2O \rightleftharpoons MgCl_2, H_2O + 5H_2O$$
$$MgCl_2 + H_2O = MgO + 2HCl.$$

The anhydrous salt can be prepared however, by heating hydrated magnesium chloride in an atmosphere of hydrochloric acid gas. It can also be prepared by the action of dry chlorine or dry hydrochloric acid gas on the magnesium metal.

Properties.—It is a colourless, deliquescent crystalline solid, highly soluble in water. Its presence in common salt makes the latter hygroscopic.

Use.—It is used for dressing cotton threads ; mixed with MgO, it is used as a cement (Sorel cement) for broken porcelain, dental stopping ; and for preparing artificial stones.

Magnesium sulphate (Epsom salt), $MgSO_4$, $7H_2O$.—It may be prepared by the action of dil. H_2SO_4 on magnesium, its oxide, hydroxide and carbonate, or upon dolomite.

Properties.—Magnesium sulphate is a *colourless*, crystalline solid, soluble in water. It loses six molecules of water of crystallisation at 150°C and become *anhydrous* at 200°C. *Unlike magnesium chloride*, therefore, we can prepare *anhydrous magnesium sulphate by heating the hydrated salt.* It forms double salts with the alkaline sulphates.

Use.—Magnesium sulphate (*Mag. Sulph.*) is used in medicine as a purgative and in cotton industry.

Magnesium nitrate, $Mg(NO_3)_2$.—It may be prepared by treating MgO, $Mg(OH)_2$, or $MgCO_3$ with dil. HNO_3.

Preparation in the Laboratory—Take dil. nitric acid in a beaker and add $MgCO_3$ to it till the effervescence, at first produced, stops. Filter and evaporate the filtrate to crystallisation.

Properties.—It is a colourless, crystalline deliquescent solid, highly soluble in water. When heated, magnesium nitrate decomposes into magnesium oxide, oxygen and nitrogen peroxide.

$$2Mg(NO_3)_2 = 2MgO + 2N_2O_4 + O_2.$$

Magnesium carbonate, $MgCO_3$.—It occurs as magnesite.

Preparation.—When a soluble carbonate is added to the solution of a magnesium salt, we do *not get* a precipitate of the *normal carbonate* but get a ppt. of the *basic carbonate.* To prepare the normal salt, the basic carbonate is suspended in water and CO_2 is passed into the liquid, when the ppt. dissolves due to the formation of magnesium bicarbonate. On now boiling the solution, normal $MgCO_3$ precipitates out.

Properties.—It is a white powder, insoluble in water. It dissolves in acids with effervescence. When heated, it decomposes into MgO and CO_2.

Use.—It is used in medicine and in preparing Epsom salt.

Detection of Magnesium

Dry test.—Magnesium compounds mixed with Na_2CO_3 and heated on charcoal in the blow pipe flame, leave a *white, incandescent* residue of MgO. This white residue on being moistened with a drop or two of cobalt nitrate solution or heated in the *oxidising* blow-pipe flame, becomes *pink* in colour.

Wet test.—(i) Ammonium hydroxide, NaOH or KOH sol. added to the solution of magnesium salt gives a white precipitate of $Mg(OH)_2$, soluble in ammonium chloride solution.

(ii) *Sodium hydrogen phosphate* solution added to the solution of a soluble magnesium salt *in presence of NH_4 salt* and $NH_4(OH)$, gives a white precipitate of *magnesium ammonium phosphate.*

Exercise

1. Name the ores of *magnesium* and give its properties and uses.

2. How will you prepare *anhydrous magnesium chloride?* Give the test for the metallic radical. *Nag., 1933; C. U., 1914, '21, '29, '43.*

3. How are *magnesium chloride* and *magnesium sulphate* prepared? *Cam. Jun.; C. U., 1911, '34, '36, '40.*

4. Starting with magnesium, how will you prepare its oxide, chloride, sulphate and hydroxide? What is dolomite? How will you prepare Epsom salt from it? Write down the preparation and uses of any two compounds of magnesium. *C. U., 1939.*

5. Describe *typical* cases of employment of electricity for extraction of metals. How is magnesium extracted?

CHAPTER XXVIII

ZINC

Symbol, Zn At. wt., 65 At. No., 30

Occurrence.—Zinc does not occur free in nature. The chief ores of zinc are *Zinc blende*, ZnS and *Smithsonite*, $ZnCO_3$, of which the former is by far the most important.

The *extraction* of zinc is effected by carbon reduction process involving following three reactions.

Concentration.—Most zinc ores particularly *Zinc blende* are concentrated by oil floatation process.

Roasting—Purified ZnS or Calamine (when the ore is the carbonate) is now roasted in air whereby it is converted into the oxide. In the case of ZnS, care is taken to see that it is transformed as completely as possible into ZnO and *not* partly into Zinc sulphate.

$$2ZnS + 3O_2 = 2ZnO + 2SO_2$$
$$ZnCO_3 = ZnO + CO_2.$$

3. **Reduction.**—The oxide is now thoroughly mixed with powdered coal (or *Anthracite*) and the mixture is heated to redness in cylindrical retorts made of fire clay by *gaseous fuel.* The retorts are closed at one end and to the open end of each retort, *after charging*, is luted a clay tube which serves as a condenser for Zinc-vapour. Quite a large number of such retorts are arranged, slightly slanting towards the mouth, in the furnace. During heating, reduction takes place ; Carbon combines with the Oxygen of Zinc oxide giving Carbon monoxide and Zinc. CO burns at the mouth of the clay tube with a *blue* flame. After a while, the flame becomes much more brilliant, showing that the metal is beginning to volatilize. A smaller condenser, made of Iron and called *prolong* (or *nozzle*), is now fitted to the end of each clay tube to complete the condensation of Zn-vapour (fig. 108). Vapour of Zinc condenses in the prolong. The molten metal is raked

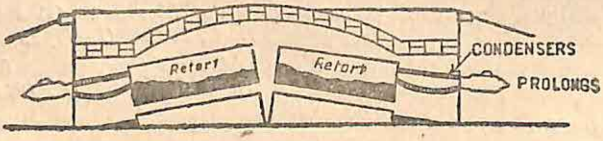


Fig. 108—Extraction of zinc

out from time to time and cast into blocks (ingots). We get commercial Zinc (*spelter*). $ZnO + C = Zn + CO$.

N. B.—The first portion of the distillate contains all the Cadmium present in the Zn ore: Cadmium, being more easily reduced and also more volatile than Zinc, distils over in the early stage.

Pure Zinc.—Commercial Zinc called *spelter*, contains Fe, Al, As, Cd, Sb as impurities. It is purified by repeated distillation.

Properties

Physical.—It is *a bluish white*, crystalline metal, brittle at the ordinary temp. At 100°—150°C it may be drawn into wire and rolled into sheets. Its sp. gr. is 6·9 and it melts at 419°C. Zinc boils at 907°C.

Chemical.—(1) *Action of air.*—Zinc is permanent in dry air but it tarnishes superficially in moist air. When strongly heated in air zinc burns with a *greenish-white* flame giving white fumes of zinc oxide called *philosopher's wool.* (2) *Action of water.*—Pure Zinc has no action on water. Water at its boiling-point is decomposed by commercial zinc. Zinc-copper couple can decompose water *slowly* at the ordinary temp. but more readily when boiled, giving off hydrogen. (3) *Action of acids.*—*Pure* zinc is almost insoluble in dil. H_2SO_4 owing to the deposit of a thin film of hydrogen which protects the surface of the metal. When the metal is *impure* hydrogen is evolved from the surface of the impurities and the metal readily dissolves in the acid. Hot and conc. H_2SO_4 attacks zinc giving off SO_2; while HCl gives hydrogen. Zinc dissolves in HNO_3 giving oxides of nitrogen or ammonium nitrate under different conditions. (4) *Action of alkalis.*—Zinc dissolves in a hot solution of caustic soda or caustic potash with the evolution of hydrogen. $Zn + 2NaOH = Zn(ONa)_2 + H_2$. (5) It precipitates copper from copper salt solution. $Zn + CuSO_4 = ZnSO_4 + Cu$.

Granulated Zinc.—Granulated zinc is prepared by pouring melted zinc in a thin stream into cold water.

Zinc-dust.—It is *bluish-grey* powder deposited in the condensers during the extraction of the metal. It is *chiefly* a mixture of zinc powder and ZnO.

Uses.—Zinc is used in electric cells: for *galvanising* iron; in preparing *alloys*; extracting gold and silver; in the preparation of gas-holders, pneumatic through, etc.

Galvanising.—It means providing articles of iron or steel with a coating of zinc. The usual method is known as *dipping* or *hot galvanising*. The article is first *thoroughly cleansed* and then dipped into a bath of *molten* zinc, the temp. being kept as low as possible. The surface of the bath is generally kept covered with a *flux* like NH_4Cl. When the article is taken out, it is found to have been coated with zinc. *Galvanising* is also called *zinc plating*.

Zinc oxide.—(*Zinc white*)—It occurs as *Red Zinc Ore.*

Prep.—It may be prepared by heating the hydroxide, nitrate or the carbonate strongly in air. $ZnCO_3 = ZnO + CO_2$.

Manufacture.—*Zinc oxide* is *manufactured* by *burning* zinc in air and then allowing the fumes to condense in suitable chambers.

$$2Zn + O_2 = 2ZnO.$$

Properties.—It is a white powder which turns *yellow when hot*, and *white when cold.* It gives a green mass when heated with cobalt nitrate solution. It is insoluble in water : but dissolves in acids producing the corresponding salts.

Uses.—Zinc oxide (*Zinc white*) is used as a pigment. It is preferred to *white lead*, for it is not blackened by H_2S ; it is also used in medicine, dentistry, and in preparing *Rinman's Green.*

Zinc hydroxide, $Zn(OH)_2$.—It is obtained as a white flocculent ppt. when NaOH sol., KOH sol. or $NH_4(OH)$ is added (*not in excess*) to the sol. of a zinc salt, like $ZnSO_4$ $ZnCl_2$, etc.

$$ZnCl_2 + 2NaOH = Zn(OH)_2 + 2NaCl.$$

Properties.—Zinc hydroxide is a white powder, insoluble in water. When strongly heated, it gives ZnO. It dissolves in acids giving salts. $Zn(OH)_2 + H_2SO_4 = ZnSO_4 + 2H_2O$. It *also* dissolves in excess of sols. of alkalis giving salts called the *Zincates.* $Zn(OH)_2 + 2KOH = Zn(OK)_2 + 2H_2O$. Zinc hydroxide therefore, is an amphoteric oxide.

Zinc chloride.—*Anhydrous* zinc chloride is obtained by heating zinc in a current of chlorine or HCl gas ; or by distilling a mixture of mercuric chloride and zinc. $HgCl_2 + Zn = ZnCl_2 + Hg$.

Hydrated zinc chloride $ZnCl_2$, H_2O is also formed by dissolving zinc, its oxide, or hydroxide or carbonate in hydrochloric acid ; evaporating and crystallising. It is usually cast into sticks.

Properties.—It is a white, very *deliquescent*, crystalline solid, highly soluble in water.

Uses.—It is used as a dehydrating agent ; for preserving timber (germ-killer) ; as a caustic in surgery ; in preparing *soldering fluids* and in dentistry.

Zinc sulphate.—(*White vitriol*, $ZnSO_4, 7H_2O$).—It is also prepared in the same way as hydrated zinc chloride by dissolving zinc, its oxide, hydroxide or carbonate in dilute H_2SO_4.

Manufacture.—It is obtained, on a large scale, by roasting *zinc blende* in air below the temp. at which it is converted into the oxide.

Zinc sulphide is converted into zinc sulphate. $ZnS + 2O_2 = ZnSO_4$ A small amount of the sulphide may escape oxidation. The mass is cooled and treated with water. Zinc sulphate dissolves but not the sulphide (if any). The *clear* solution is taken off and evaporated.

ZnS (roasted)→mass (water)→solution (evaporated)→$ZnSO_4, 7H_2O$

Properties.—Zinc sulphate is a colourless, crystalline solid having the formula $ZnSO_4, 7H_2O$. It slowly effloresces when exposed to the air, and becomes anhydrous when heated to 300°C. It is soluble in water. It is isomorphous with Epsom salt.

Uses.—It is used in medicine and in dyeing.

Zinc nitrate, $Zn(NO_3)_2$.—It is prepared by dissolving zinc or its oxide, hydroxide or carbonate in dilute HNO_3.

Properties.—It is a *colourless*, very deliquescent crystalline solid, highly soluble in water. When heated strongly, it decomposes into zinc oxide, nitrogen dioxide and oxygen.

Zinc carbonate, $ZnCO_3$.—It occurs as *Calamine*, *Smithsonite*, or *Zinc spar*.

Preparation.—When the sol. of a metallic carbonate is added to the sol. of a zinc salt, we get a ppt. of the *basic carbonate of* zinc. The normal salt is obtained as a white ppt. by the action of a soluble *bicarbonate*, like $NaHCO_3$, on the sol. of a zinc salt.

Properties.—It is a white solid, insoluble in water, but dissolves in acids.

Zinc Sulphide, ZnS.—It occurs as zinc ore under the name zinc blende. It can be obtained as a white precipitate by adding ammonium sulphide to a solution of zinc salt.

$$ZnSO_4 + (NH_4)_2S = ZnS + (NH_4)_2SO_4$$

It is a white solid insoluble in water but soluble in dilute mineral acids liberating H_2S.

Uses.—It is used as a luminous paint and in the manufacture of lithophane. Lithophane is a white pigment of wood-covering power not blackened by H_2S. Lithophane is obtained by co-precipitating ZnS and $BaSO_4$ by the action of barium sulphide on zinc sulphate solution. $ZnSO_4 + BaS = ZnS + BaSO_4$.

Detection of Zinc

Dry Test.—Compound of Zinc, mixed with Na_2CO_3 and heated on charcoal under the blow pipe flame, leave an incandescent residue which is *yellow* when hot and *white* when cold. The residue, on being moistened with cobalt nitrate sol. and heated in the *oxidising* blow-pipe flame turns *green* (—*Rinman's Green*).

Wet Test.—(i) Ammonium sulphide gives a white precipitate of ZnS with the solution of a zinc salt. The ppt. is soluble in acids.

(ii) Sol. of zinc salt in water gives a white precipitate of $Zn(OH)_2$ with NaOH, KOH or $NH_4(OH)$ sol. which dissolves in excess of the alkali.

Exercise

1. Mention the principal ores of zinc and state how the metal is obtained. Describe its properties and chief uses. How will you prepare white vitriol ?

C. U., I. Sc. 1959.

2. What is the action of (*a*) caustic soda, (b) sodium carbonate and (*c*) Water on metallic Zinc ? *C. U., I. Sc., 1959.*

3. Name an important ore of Zinc with its formula. Give outlines of the extraction of the metal from the ore. State its important uses.

Explain with equations what happens when :—

(*a*) Zinc is added to Copper Sulphate Solution.

(*b*) Zinc is headed with Caustic Soda Solution. *Cal. Pre-U., 1962, '65.*

4. Name and write formula of an important ore of Zinc. Give a short account of the extraction of the metal from the ore, stating clearly the reactions with equations, involved. State two important uses of the metal. Describe with equations the action of (*a*) Sodium hydroxide, (*b*) Copper Sulphate Solution on Zinc.

Cal. Pre-U. 1967.

5. Name the important ores of zinc and describe the extraction of the metal from its ore. *Cal. Pre-U., 1970.*

CHAPTER XXIX

MERCURY

Symbol, Hg At. wt., 200 At. No. 80

Occurrence—It occurs in the free state and as cinnabar, HgS.

Extraction.—Mercury is extracted from its ore, cinnabar by simultaneous roasting and distillation. First of all, mercuric oxide is produced which then decomposes by heat into mercury and oxygen. Mercury distils over and is condensed.

$$2HgS + 3O_2 = 2HgO + 2SO_2 \parallel 2HgO = 2Hg + O_2$$

Mercury thus obtained is not pure. It contains metallic impurities like Zn, Sn, Pb, Bi, etc. dissolved in it.

Purification of Mercury.—The metal is purified (1) from suspended inpurities by filtering it through chamois leather ; and (2) from soluble impurities (*a*) by running it *several times* in a thin stream through a long column of dilute HNO_3 and then (*b*) by distilling it in a vacuo.

Properties

Physical.—Mercury, also called *Quicksilver*, is a silver-white metal, liquid at the ordinary temp. It solidifies at −39°C and boils at

357·25°C. In the vaporous state a *molecule of mercury consists of one atom.* The metal gives off vapours even at the ordinary temperature.

Chemical.—(1) *Action of air.*—Mercury is not attacked by air, either dry or moist, at the ordinary temp. When heated in air, near boiling-point, mercury slowly combines with oxygen to form the *red oxide* of mercury. (2) *Action of water.*—Mercury is not attacked by water at any temp. (3) *Action of acids.*—It is not attacked by HCl (*dil.* or *conc.*). Conc. H_2SO_4 has no action on mercury in *cold*, but mercury is attacked by *hot* and *conc.* H_2SO_4 with the evolution of sulphur dioxide. $Hg + 2H_2SO_4 = HgSO_4 + 2H_2O + SO_2$

Mercury dissolves in nitric acid, giving oxides of nitrogen.

(4) *Action of alkalis.*—It is not attacked by alkalis. (5) It forms *amalgams* with many metals (except Fe and Pt). (6) It is attacked by halogens, and combines directly with sulphur.

Uses.—It is used in the construction of some physical and chemical apparatus like thermometers, barometers, etc : for silvering mirrors ; for collecting gases ; for making amalgams ; in extracting gold and silver ; and for preparing mercury compounds.

Mercurous oxide, Hg_2O.—Prep.—It is obtained as a dark-grey ppt. when NaOH or KOH sol. is added to the sol. of a mercurous salt.

$$Hg_2(NO_3)_2 + 2NaOH = Hg_2O + 2NaNO_3 + H_2O.$$

Properties—It is a dark-grey powder, insoluble in water.

Mercuric oxide, HgO—It exists in two different varieties : *red* crystalline solid, and *yellow* amorphous powder.

Preparation.—The red crystalline variety is obtained in the *dry way* either by heating mercury for a long time, near its boiling-point in contact with air ; or by carefully heating mercuric nitrate alone or intimately mixed with mercury. $Hg + Hg(NO_3)_2 = 2HgO + 2NO_2$.

The yellow variety is obtained in the *wet way*. When the solution of mercuric salt is treated with caustic soda or caustic potash solution, a yellow ppt. of HgO is obtained.

$$HgCl_2 + 2NaOH = HgO + H_2O + 2NaCl.$$

Properties.—Mercuric oxide is a red crystalline solid or a yellow amorphous power. The yellow powder becomes red when heated to 400°C. With the rise of temp. the colour changes from red to black till HgO begins to decompose into mercury and oxygen. The red colour reappears on cooling. Mercuric oxide is insoluble in water, but dissolves in acid to give mercuric salts.

Mercurous chloride (Calomel), Hg_2Cl_2.

Preparation.—This compound is obtained as a curdy, white precipitate when the solution of a soluble mercurous salt is treated with HCl or with the solution of a chloride.

$$Hg_2(NO_3)_2 + 2HCl = Hg_2Cl_2 + 2HNO_3.$$
$$Hg_2(NO_3)_2 + BaCl_2 = Hg_2Cl_2 + Ba(NO_3)_2.$$

Manufacture.—In the dry way, it is manufactured by heating an intimate mixture of mercuric chloride and mercury in an almost closed vessel, when Hg_2Cl_2 formed sublimes off and condenses as a white cake. The sublimate is repeatedly boiled with water (*to completely* free it from mercuric chloride), filtered and then dried.

$$HgCl_2 + Hg = Hg_2Cl_2.$$

Properties.—It is an amorphous, tasteless, white powder, insoluble in water and in dilute acids. It sublimes unchanged when heated. It dissolves in *aqua regia* to form $HgCl_2$. It is *blackened* by ammonia due to the formation *possibly* of a mixture of Hg and NH_2HgCl.

Use.—Calomel is used in medicine as a purgative.

Mercuric chloride (Corrosive sublimate), $HgCl_2$.

Preparation.—The substance is formed when chlorine is passed over heated mercury. Corrosive sublimate can also be prepared by dissolving either mercury or calomel in *aqua regia*.

Manufacture.—Mercuric chloride is manufactured by heating a mixture of mercuric sulphate and common salt in long-necked flat-bottomed flasks on a sand bath. $HgSO_4 + 2NaCl = HgCl_2 + Na_2SO_4$. A little MnO_2 is added to prevent the formation of calomel. After the reaction on cooling, the flasks are broken and the cake of mercuric chloride condensed on the upper part, is removed. It is purified by recrystallisation from solution in water.

Properties.—Corrosive sublimate is a white, needle-shaped, crystalline solid, soluble in water, but more so in ether and in alcohol. It is extremely poisonous. Albumen (white of eggs) forms an insoluble compound with it, and is, therefore, used as an antidote. It is reduced by stannous chloride first into calomel, and then with more stannous chloride, into mercury.

$$2HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4$$
$$Hg_2Cl_2 + SnCl_2 = 2Hg + SnCl_4.$$

Mercuric chloride solution gives a *white precipitate*—called *infusible* *white precipitate* (NH_2HgCl)—with ammonia ; and a red precipitate of mercuric iodide with potassium iodide solution.

$HgCl_2 + NH_3 = NH_2HgCl + HCl \parallel HgCl_2 + 2KI = HgI_2 + 2KCl$

Uses.—It is used in medicine as an antiseptic ; and in dressing skins, furs, etc.

Mercurous nitrate, $Hg_2(NO_3)_2$—It if formed when dil. HNO_3 reacts with excess of mercury *in cold*. The solution yields crystals on standing. Mercury is always kept in the solution *in excess* to prevent oxidation of mercurous nitrate into the mercuric compound.

Properties.—It is a colourless, crystalline solid, containing two molecules of water of crystallisation. It is soluble in water.

Mercuric nitrate, $Hg(NO_3)_2$—It is prepared by boiling mercury with excess of conc. HNO_3 till the solution gives no ppt. of Hg_2Cl_2 with common salt. The solution is now allowed to evaporate over conc. H_2SO_4 in a desiccator, when deliquescent crystals having the composition $2Hg(NO_3)_2, H_2O$ separate out.

It can also be prepared by dissolving mercuric oxide, HgO in HNO_3.

Properties.—It is a colourless, deliquescent, crystalline solid. When heated, it gives mercuric oxide which on further heating, decomposes into Hg and O_2. It is soluble in water.

Mercurous sulphate, Hg_2SO_4—It is obtained as a white precipitate, when dil. H_2SO_4, or a soluble sulphate is added to the solution of a mercurous salt. $Hg_2(NO_3)_2 + Na_2SO_4 = Hg_2SO_4 + 2NaNO_3$.

Properties.—It is a heavy, white crystalline solid, very slightly soluble in water.

Mercuric sulphate, $HgSO_4$—**Prep.**—Boil mercury with one-and-half times its weight of conc. H_2SO_4 and evaporate the solution to dryness. $Hg + 2H_2SO_4 = HgSO_4 + 2H_2O + SO_2$.

It may also be obtained by dissolving mercuric oxide in sulphuric acid. $HgO + H_2SO_4 = HgSO_4 + H_2O$

Properties.—It is a white, crystalline solid. It is decomposed by water into tne basic sulphate.

Mercuric sulphide, HgS.—It is the only sulphide of mercury known. Mercurous sulphide has not been prepared.

Vermilion.—Used as a paint—is also mercuric sulphide. *Vermilion* is obtained by triturating (rubbing in a mortar) mercury and *flower* of sulphur with a little KOH solution. The mixture is heated to 45°C with more KOH sol. till the colour changes from *black* to bright *red*. HgS is then poured into water, washed and dried.

In the laboratory, mercuric sulphide is formed when H_2S is passed through the solution of a mercuric or mercurous salt. In the former case, the ppt. obtained is first *white*, then it turns *yellow*, then *brown* and finally *black* in colour. In the latter case, we immediately get a black ppt. of a mixture of HgS and Hg.

$$Hg(NO_3)_2 + H_2S = HgS + 2HNO_3.$$
$$Hg_2(NO_3)_2 + H_2S = HgS + 2HNO_3 + Hg.$$

Properties.—It is a deep red crystalline solid, insoluble in water and in acids. It dissolves in *aqua regia* giving mercuric chloride. When HgS is heated in air, we get vapours of mercury and SO_2.

Use.—Mercuric sulphide prepared by special mathod is used in medicine as Makaradhwaja, Rasasindura, etc. *Vermilion*, which is also mercuric sulphide, is used as a paint.

Detection of Mercury

Dry Test.—Compounds of mercury heated with Na_2CO_3 and charcoal powder in a bulb-tube, readily deposit a beautiful mirror of mercury on the cold surface of the tube.

Cu-foil or Cu-turnings Test.—To prove that *any* soluble compound of Hg contains Hg, introduce Cu turnings into the sol of the compound, when Hg is deposited on Cu. Take out Cu-turnings, wash and dry them. Now heat them in a *dry* test tube. Mercury vaporises off and is deposited on the cold side of the test tube.

Exercise

1. Name the compounds of mercury with chlorine. How are they manufactured? Describe their properties and give two tests of each. How will you detect $HgCl_2$ present in Hg_2Cl_2 as an impurity?

2. How does mercury occur in nature? What is its most important ore? How is the metal extracted and purified? Name a few of its important compounds with formulae. Describe the properties and uses of the metal and three of its compounds. Prove that $HgCl_2$ contains Hg.

3. Starting from mercuric chloride how would you prepare mercurous chloride, mercuric oxide and mercury? Give one test each for the Hg compounds in the *dry* and *wet* ways.

CHAPTER XXX

ALUMINIUM

Symol, Al At. wt., 27 At. No., 13

Occurrence—Aluminium is widely distributed in nature ranking third among the elements found in the earth's crust. It is a constituent of many substances which go to make up the primary rocks—felspar, zeolite, mica etc. Those substances are mainly complex silicates. The weathering of these rocks produces clay which contains much aluminium.

In the form of anhydrous oxide, Al_2O_3, it occurs in corundum and emery. Precious gems such as ruby (red-*Chuni*), sapphire (blue-*Neelum*), emerald (green-*Panna*) are nothing but crystals of corundum tinted in beautiful colours by traces of foreign oxides.

Of all the minerals of aluminium, bauxite, Al_2O_3, $2H_2O$ is the most important, for it is the only one from which aluminium is extracted today. Cryolite, AlF_3, $3NaF$ is much used in aluminium metallurgy,

Aluminium is found in different parts of India—in Bihar, Madhya Pradesh, at Katni and in the States of Bombay and Madras.

Aluminium metal was first isolated in 1827 by Wohler, but the commercial method now used for the extraction of aluminium by electrolysis of aluminium oxide dissolved in cryolite was discovered in 1886 by Charles Martin Hall, a young American student and Paul Heroult, a Frenchman independently when they were both only twenty two years old.

Hall and Heroult's Electrolytic process for the extraction of Aluminium.

The method consists of two steps—(1) Purification of the bauxite and (2) Electrolysis of the purified bauxite..

(1) **Purification of the Bauxite.**—The Bauxite contains many impurities such as Fe_2O_3, TiO_2, SiO_2 etc. It has to be purified before electrolysis which is generally done by more than one processes, of which one is described below.

Bayer Process.—It is followed when bauxite contains little SiO_2 but much Fe_2O_3 as impurities. Bauxite is finely ground and calcined below red heat, and the calcined mass is digested with NaOH sol. (45% strength) under 80 lb. p.s.i. pressure at 150°C, when Al_2O_3 goes into sol. as sodium aluminate, while Fe_2O_3, $Fe(OH)_3$, etc. remain insoluble. Sodium aluminate sol. is now diluted, filtered, and the filtrate is taken off and digested with a little $Al(OH)_3$ with constant agitation. $NaAlO_2$ is thereby hydrolysed and the whole of aluminium precipitates out as $Al(OH)_3$. It is now removed, washed and ignited. We get alumina Al_2O_3.

$$Al_2O_3 + 2NaOH = 2NaAlO_2 + H_2O$$
$$2NaAlO_2 + 4H_2O = 2Al(OH)_3 + 2NaOH$$
$$2Al(OH)_3 = \underset{\text{Alumina.}}{Al_2O_3} + 3H_2O$$

(2) **Electrolysis of Purified Bauxite.**—Bauxite, thus purified is now dissolved in *fused* cryolite and *electrolysed* in an electric furnace. The furnace consists of an iron box lined with carbon, which is made the *cathode*. The *anode* consists of stout carbon rods attached to a rod of copper. The carbon rods are suspended in the molten bath as in fig. 109. A little fluorspar is added to increase the fluidity of the bath which is kept covered with a layer of charcoal. When electric

current is passed in, the resistance of the electrolyte gives sufficient heat to keep the mass in the *fused state* (900°C), and aluminium oxide is decomposed. Aluminium is liberated at the *cathode*, and the metal

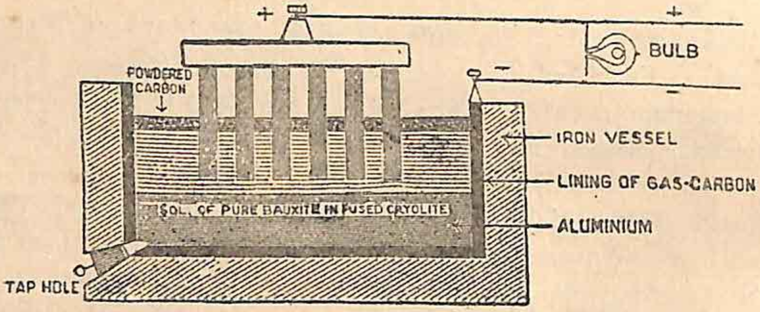


Fig. 109—Extraction of aluminium (99 per cent) from purified bauxite

n the liquid state sinks to the bottom whence it is taken out by means of the 'tap hole'. Oxygen, liberated at the *anode*, attacks the carbon rods producing CO and CO_2 which are given off.

N. B.—The method is continuous. When Al_2O_3 is exhausted the resistance of furnace increases. The current now flows through a lamp, shunted off the circuit. The lamp glows. More Al_2O_3 is now added.

Properties

Physical.—It is white metal with a bluish tinge. It melts at about 658°C. It is malleable, ductile, and very light ; but it possesses great toughness and tensile strength. Its sp. gr. is about 2·7. It is a good conductor of heat and electricity.

Chemical.—(1) *Action of air.*—Dry air has no action ; moist air produces a thin film of the oxide which protects the metal from further action. When strongly heated in air, it burns brilliantly giving Al_2O_3 (2) *Action of water.*—Al-foil or Al-powder decomposes water at 100°C. giving off H_2 and is slowly converted into $Al(OH)_3$. Aluminium dissolves in saline solutions. (3) *Action of acids.*—HCl (dil. or conc.) reacts with the metal giving off H_2. Hot and conc. H_2SO_4 attacks aluminium with the liberation of SO_2. Nitric acid, dilute or concentrated has very little action on aluminium. (4) *Action of alkalis.*—Aluminium rapidly dissolves in a hot solution of $NaOH$ or KOH with the evolution of hydrogen and the formation of the aluminate $Al+2KOH+2H_2O=2KAlO_2+3H_2$. (5) When heated with the halogens, aluminium gives the halides, while heated in nitrogen, it forms the nitride, AlN. (6) Al reduces the oxides of Fe, Cr, Mn, Si., when they are mixed with the powdered solid and are strongly heated.

$$Fe_2O_3 + 2Al = 2Fe + Al_2O_3 \quad \| \quad 3SiO_2 + 4Al = 2Al_2O_3 + 3Si.$$

Goldschmidst's Thermite process.—Thermit is a mixture of Fe_2O_3 and Al-powder. It is used in welding broken iron rails, parts of shfps, etc.

Aluminium Oxide or Alumina, Al_2O_3, occurs as corundum and emery and also as gems such as ruby, sapphire, emerald etc., the colour of which is due to traces of impurities.

Aluminium oxide is prepared by strongly heating aluminium hydrooxide or alum. $2Al(OH)_3 = Al_2O_3 + 3H_2O$.

It is an amphoteric oxide, white in colour. It dissolves both in acids and alkalis. Ignited Al_2O_3 is, however, insoluble in all acids including aqua regia.

Use.—Corundum is highly valued and used for grinding emery is used for polishing purposes.

Aluminium hydroxide, $Al(OH)_3$—Preparation—It is obained as a white *gelatinous* ppt. by adding $NH_4(OH)$ to the solution of an aluminium salt.

Properties.—It dissolves in acids giving aluminium salts.

$$Al(OH)_3 + 3HCl = AlCl_3 + 3H_2O$$

and it also dissolves in KOH or NaOH sol. producing **aluminate.**

$$Al(OH)_3 + NaOH \rightleftharpoons NaAlO_2 + 2H_2O.$$

When heated strongly, it gives Al_2O_3. Precipitated $Al(OH)_3$ possesses the properties of (i) carrying down colloidal substances with it, and (ii) uniting with many soluble organic colouring matters.

Uses.—It is used (i) indirectly for purifying drinking water (ordinarily *alum* or *ferro-alum* is utilised for the purpose) and (ii) as a mordant in dyeing industry.

Anhydrous aluminium chloride is prepared by the action of chlorine or hydrochloric acid gas on aluminium. $2Al + 6HCl = 2AlCl_3 + 3H_2$.

In the hydrated form, $(AlCl_3, 6H_2O)$, it is obtained by dissolving aluminium, aluminium oxide or hydroxide in hydrochloric acid and evaporating the solution to crystallisation.

Commercially, anhydrous aluminium chloride is obtained by passing chlorine gas over a mixture of Al_2O_3 and carbon.

$$Al_2O_3 + 3C + 3Cl_2 = 2AlCl_3 + 3CO$$

Aluminium chloride is a white crystalline substance and in the anhydrous form it is much used in organic synthesis.

Aluminium Sulphate, $Al_2(SO_4)_3$, $18H_2O$.—It is prepared by heating bauxite with sulphuric acid. When aluminium sulphate solution is treated with requisite quantity of potassium sulphate solution and the solution is evaporated to crystallisation, we get potash alum, K_2SO_4, $Al_2(SO_4)_3$, $24H_2O$.

Alum—By alum, we ordinarily mean potash alum. K_2SO_4, $Al_2(SO_4)_3$, $24H_2O$. In a broader sense it refers to isomorphous double sulphates having the general formula, R_2SO_4, $M_2(SO_4)_3$, $24H_2O$ where R is an atom of a monovalent element (K, Na, Ag) and M is an atom of a trivalent element (Al, Cr, Fe)

Potash Alum, or ordinary or common alum (Fatkiri), K_2SO_4. $Al_2(SO_4)_3$, $24H_2O$.—**Preparation**.—Alum is made commercially by dissolving powdered bauxite in hot conc. sulphuric acid (62%) in lead-lined vessels. The solution is then treated with barium sulphide to reduce ferric sulphate to ferrous sulphate. The solution is filtered and then requisite quantity of potassium sulphate is added. On concentration and cooling, alum crystals K_2SO_4,. $Al_2(SO_4)_3$, $24H_2O$ are obtained which are freed from iron impurities by recrystallisation.

Properties.—It is a colourless, crystalline solid soluble in water. Like all other alums it is less soluble than the single sulphate. Hence it can be obtained in a greater degree of purity than the single sulphate. The solution in water is acidic and has no astringent taste.

When left exposed to the air, alum becomes coated with a white efflorescence due to the absorption of ammonia and formation of a basic sulphate. When heated, alum first melts in its water of crystallisation : on still further heating, it undergoes decomposition till, at last, a white porous mass is left, known as *burnt* alum.

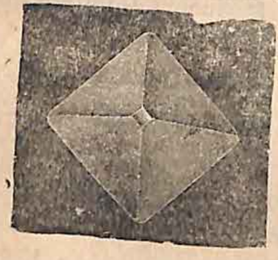


Fig. 110—Alum crystals

Uses.—It is used in dyeing industry ; in calico-printing ; in medicine ; in tanning ; and for purifying water.

Aluminium nitrate, $Al(NO_3)_3$, $9H_2O$.—It is obtained by dissolving $Al(OH)_3$ in dil HNO_3 and evaporating the sol. to crystallisation. It is a deliquescent crystalline solid, highly soluble in water. When heated, it breaks up into Al_2O_3, N_2O_4 and oxygen.

Detection of Aluminium

Dry Test—Compounds of aluminium heated on charcoal under the blow-pipe flame, leave a white incandescent mass. The mass, on being moistened with cobalt nitrate solution and re-heated in the oxidising flame, is coloured *blue* (—*Thenards blue*).

Wet Test.—NaOH, KOH or $NH_4(OH)$ solution added to the solution of a soluble aluminium salt gives a white gelatinous pp. of $Al(OH)_3$. The ppt. is *insoluble* in NH_4Cl sol. but dissolve in excess of NaOH or KOH sol. On treating or boiling this sol (*i.e.*, of *sodium* or *potassium aluminate*) with NH_4Cl, $Al(OH)_3$ is again precipitated.

Exercise

1. How will you prepare aluminium chloride, alum, alumina and aluminium hydroxide? *Mad., 1929 ; All., 1926.*

2. Describe briefly the electrolytic process for the extraction of aluminium. What is the Thermit process ? What is an alum ?
All., 1991 ; Punj., 1933 ; Mad., 1930, Banaras, 1930, '35 ; C. U., 1930, '35, '45, '47, '49, '51.

3. What is an alum ? Name the principal alums and give the properties and uses of any one of them. *C. U., 1921, '22, '24, '28, '41.*

4. Name an important ore of aluminium with its formula. Give outlines of the extraction of the metal from the ore. State its important uses. *Cal Pre-U., 1961.*

5. What is the chief natural source of aluminium ? How is the metal extracted from it ? Give outlines only. State the properties and uses. *Cal. Pre-U., 1964.*

6. State with equation what happens when Aluminium is heated with 30% Potassium Hydroxide.

Name and write the formulae of the important ores from which Aluminium is obtained. *Cal. Pre-U., 1965.*

7. Name and write formula of an important ore of aluminium. Describe in outline the method of extraction of aluminium from the ore. How is Potash alum prepared. What are its important uses ? *Cal. Pre-U., 1966.*

CHAPTER XXXI

Tin

Symbol, Sn At. wt., 119. At. No., 50.

Tin, which is required to prepare bronze, is known since pre-historic time.

Occurrence.—The most important ore of tin is *Tinstone* or *Cassiterite*, SnO_2.

Extraction.—Preliminary concentration of the tinstone is effected first (i) by calcining to remove sulphur and arsenic impurities as SO_2 and As_4O_6 (arsenious oxide) and then (ii) by washing with water to remove Cu and Fe impurities mainly converted into their sulphates and oxides during calcination. The soluble sulphates dissolve and lighter oxides are washed away, heavy tinstone falling to the bottom. Wolfram, if present, is removed by electro-magnetic separation.

The tinstone is then reduced with carbon. $SnO_2 + 2C = Sn + 2CO$.

Refining of crude tin is carried out in two stages.

(i) **Liquation.**—The crude metal is melted on the bed of a reverberatory furnace, when easily fusible tin flows away from the impurities, Cu, Fe, As etc.

(ii) **Poling.**—The liquated tin is fused in a pot and stirred with green poles of wood. Hydrocarbons evolving from the poles of wood keeps the molten mass agitated thereby exposing it to the oxidising action of the air. The impurities like iron are oxidised and separated as a scum which is removed. We get commercially pure tin.

Properties

Physical.—Tin is a white metal with a brilliant lustre and a sp. gr. of 7·3. It is soft and malleable, so that it can be hammered out into thin foils (*tin-foils*). It becomes brittle when heated to 200°C. The metal melts at 232°C. When a bar of tin is bent, it emits a peculiar noise, called the *cry of tin*. When ordinary tin is cooled *below* 18°C, it crumbles down to a grey powder, which is an allotropic from of the metal and is called *Grey tin*.

Chemical.—(1) *Action of air.*—Dry air has no action on the metal. It also remains unchanged in air at the ordinary temperature. At white heat (1500°C – 1600°C), it burns in air with a white light giving SnO_2, (2) *Action of water.*—Tin is not attacked by water, especially when both are pure. (3) *Action of acid.*—It dissolves slowly in hydrochloric acid forming stannous chloride and liberating hydrogen. $Sn + 2HCl = SnCl_2 + H_2$. Tin is only slowly attacked by cold dil. H_2SO_4 giving $SnSO_4$ and evolving H_2 ; hot conc. H_2SO_4 dissolves the metal readily giving stannic sulphate, $Sn(SO_4)_2$ (with some basic salts) and SO_2. Cold and dil. HNO_3 reacts with tin giving stannous nitrate and ammonium nitrate.

$$4Sn + 10HNO_3 = 4Sn(NO_3)_2 + 3H_2O + NH_4NO_3.$$

Pure and highly conc. nitric acid (sp. gr. 1·52) has *no action on tin*. The metal dissolves in *aqua regia* giving stannic chloride. (4) *Action of alkalis.*—Tin dissolves in hot conc. KOH or NaOH solution giving potassium or sodium stannate, and hydrogen is set free.

$$Sn + 2KOH + H_2O = K_2SnO_3 + 2H_2.$$

Uses.—It is used for preparing alloys ; in preparing vessels of household and technical use ; for the manufacture of tin-foils : for '*tinning*' (or *tin*-plating) copper and iron articles ; tin amalgam is sometimes used in the manufacture of mirrors.

Tin occurs in allotropic forms as grey tin, white tin (ordinary tin) and rhombic tin.

Alloys of Tin.—Common alloys of tin are : (1) *Pewter.*—It is an alloy of tin (4 parts) and lead (1 part) : (2) *Soft solder.*—It is an alloy of lead (1 part) and tin (1 part) ; (8) *Gun metal*, *Speculum metal*, etc.,—they are alloys of Cu and Sn.

Tinning or Tin-plating.—Metals like iron, copper, and alloys like brass, etc. are tinned by dipping the heated metals into a bath of molten tin whereby a thin coating of tin is produced on their surface. Tinning may also be effected by rubbing the surface of the heated metal with NH_4Cl and molten tin.

Tin plates are thin sheets of mild steel provided with a coating of tin on the surface. The steel plates are first *pickled* with dilute H_2SO_4 and finally washed. They are now dipped into baths of molten tin to which fused $ZnCl_2$ is added to avoid the formation of tin oxide. The plates are taken out and passed through palm oil.

Uses of Tin plates.—They are used in the manufacture of tin canisters, trunks, cans, boxes, etc. ; for canning meat, fruits ; and in manufacture of vessels for storing petroleum.

There are two oxides of tin—(1) *Stannous oxide*, SnO and (2) *Stannic oxide*, SnO_2, the former is a black powder, insoluble in water but soluble in acids. The latter occurs in nature as *tinstone*. Stannic oxide is a white solid insoluble in water as well as in acids.

Stannous chloride is the most important compound of tin. The anhydrous salt is prepared by heating tin in dry hydrochloric acid gas. The hydrated salt is readily prepared by dissolving tin in conc. hydrochloric acid. $Sn + 2HCl = SnCl_2 + H_2$,

On evaporation the salt crystallises out with two molecules of water of crystallisation, $SnCl_2, 2H_2O$ and is known as *Tin salt*.

Properties.—It is a colourless crystalline substance, soluble in water. With excess of water, it undergoes hydrolysis giving a white ppt. of the oxychloride of tin. $SnCl_2 + H_2O = Sn(OH)Cl + HCl$. It is a powerful reducing agent. It reduces mercuric chloride into insoluble mercurous chloride which is thrown down as a white ppt. On boiling with excess of $SnCl_2$ mercurous chloride first formed is further reduced to mercury, the ppt. turning grey.

$$2HgCl_2 + SnCl_2 = \downarrow Hg_2Cl_2 + SnCl_4$$
$$Hg_2Cl_2 + SnCl_2 = 2Hg + SnCl_4$$

Uses.—It is used in dyeing industry and as a reducing agent.

Stannic chloride, $SnCl_4$.—It is obtained as a colourless liquid when chlorine is passed into molten tin. $Sn + 2Cl_2 = SnCl_4$

Stannic sulphide, SnS_2—also known as *mosaic gold* is prepared in the dry way by heating together tin amalgam, sulphur and ammonium chloride in retort. Mosaic gold is used in cheap gilding.

Detection of Tin

Dry Test.—(i) Tin compds. heated on charcoal with Na_2CO_3 and KCN under the reducing blow-pipe flame, yield malleable, white metallic *scattered* beads which do not mark-paper. When the beads are dissolved in dil. HCl and the solution of $SnCl_2$ thus obtained, is treated with a mixture of $K_3Fe(CN)_6$ and $FeCl_3$ solutions, wet get a *blue* ppt.

Borax-bead test.—Borax-bead, coloured *blue* by Cu-salts, turns *red* in the *oxidising* flame in presence of tin or *stannous* salts.

Wet Test.—When H_2S gas is passed into the solution of a stannous salt, a chocolate brown ppt. of SnS is obtained which is soluble in yellow Am. sulphide. With a stannic salt a yellow ppt. of SnS_2 soluble in yellow Am. sulphide is obtained.

Exercise.

1. From what source and how is the metal tin obtained in the pure state? What is *cry of tin*? *Bom., 1934., Punj., 1933 : Mad., 1931*

How is *mosaic gold* prepared? *C. U., 1941*

2. Starting with tin how will you prepare—*(a)* $SnCl_2$. *(b)* $SnCl_4$ *(c)* SnS and *(d) Pewter*? How are articles *tinned* and why? What is the action of HNO_3 on Tin? *Patna., 1919; Mad., 1919 : C. U., 1931, '39, '45.*

CPAPTER XXXII

LEAD

Symbol, Pb. At. wt., 207·1 At. No., 82.

History.—Leat was known to the ancient Egyptian.

Occurrence.—Traces of Lead are occasionally found in nature in the free state. In combination, it occurs—

(1) *as Sulphide*, **Galena, PbS**, (2) *as Sulphate*, **Anglesite, $PbSO_4$**, (3) *as Carbonate*, **Cerussite, $PbCO_3$**, (4) *as Chloride*, **Matlockite $PbCl_2$, PbO.**

Two processes are generally employed.

(1) *Air reduction process.* (2) *Carbon reduction process.*

(1) *Air reduction process.*—

There are two steps in this process :

(a) *Roasting.*—The ore is roasted in a reverberatory furnace at temperature at which it is partly converted into oxide and partly into sulphate, a part again remaining unchanged. (fig. 111).

$$2PbS + 3O_2 = 2PbO + 2SO_2$$
$$PbS + 2O_2 = PbSO_4$$

(b) *Smelting.*—The roasted mass is then heated to bright red heat in the reverberatory furnace with a little quicklime.

The following reactions take place with the production of lead.

$$PbS + 2PbO = 3Pb + SO_2 \quad \| \quad PbS + PbSO_4 = 2Pb + 2SO_2$$

(2) *Carbon reduction process.*—

In this process, the ore which is generally a poor one is powdered and then concentrated by oil floatation process. The concentrated

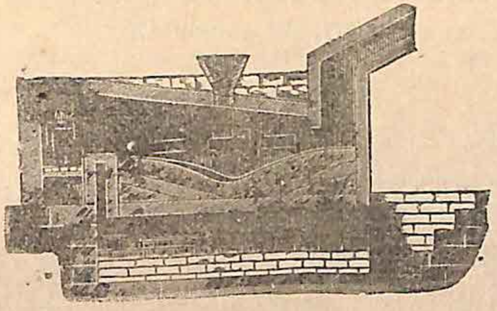


Fig. 111—Extraction of lead from galena

ore is then roasted in a pot with a view to convert it mainly into lead oxide, some lead sulphate being produced at the same time. The powdered ore by superficial melting, forms a compact mass which is then broken up into lumps of suitable size. These lumps along with coke, some haematite iron ore and limestone are then charged into a small blast furnace.

The reduction of the lead oxide is mainly brought about by carbon monoxide. Some of the reactions taking place in the blast furnace leading to the production of lead metal are noted below.

$$C+O_2=CO_2 \quad \| \quad CO_2+C=2CO$$

$$PbO+C=Pb+CO \quad \| \quad PbS+PbSO_4=2Pb+2SO_2$$

Ferric oxide is also reduced to iron which sets free lead from lead sulphide. $Fe_2O_3+3CO=2Fe+3CO_2$ ‖ $PbS+Fe=Pb+FeS$

Iron sulphide forms a layer on the molten lead. The molten lead is withdrawn from the tap hole at intervals.

Softening of Lead.—Lead obtained from galena whether by the air-reduction process or by smelting with coke in a blast furnace, is not pure. It still contains small quantities of silver, antimony, arsenic, iron, zinc, copper bismuth, sulphur, etc. as impurities and is hard. Pure lead is soft. The impure metal is freed from all the impurities, *except silver*, by being melted on the hearth of reverberatory furnace until the impurities are oxidised and form a scum on the surface. The scum is removed from time to time and the process is continued till lead shows the proper degree of *softness*.

Softening of lead, therefore, means *removal of impurities present in commercial lead and making it literally soft.*

Desilverising of Lead.—*Softened* lead still contains silver. It is desilverised by Parkes and Pattinson processes.

Thus, we see that lead for the market is *necessarily* very pure. It is purified not so much on its own account as on account of the valuable. impurities like silver, antimony, etc. present in it.

Properties

Physical.—Lead is a lustrous metal of bluish-grey colour. It can be cut with a knife, and it *marks paper*. It possesses little tenacity. Its sp. gr. is 11·36, and it melts at 326°C.

Chemical—(1) *Action of Air.*—Perfectly dry air has no action on the metal. Exposed to moist air, its bright metallic lustre disappears and a thin layer of the oxide, and ultimately of the basic carbonate is deposited on the surface. When strongly heated in air or in oxygen, it is converted into litharge.

(2) Action of water on lead—

Pure distilled water appears to have no action on lead in absence of air. But water containing air and also substances such as nitrates, ammonium salts etc., (which tend to form soluble compounds of lead) dissolves lead. Soluble compounds of lead are cumulative poison and hence the risk of conveying water through lead pipes. But hard water has got no dissolving action on lead and therefore it can safely be carried through lead pipes,

(3) *Action of acids.*—Lead is little affected by dil. HCl or dil. H_2SO_4. The hot conc. acids attack lead, but the action slows down, due to the formation of a crust of insoluble lead chloride or sulphate on the surface, which protects the metal from further action. $Pb + 2H_2SO_4 = PbSO_4 + 2H_2O + SO_2$. Nitric acid of all concentrations attack the metal giving led nitrate and oxides of nitrogen. $Pb + 4HNO_3 = Pb(NO_3)_2 + 2H_2O + 2NO_2$. Lead is also dissolved by organic acids like acetic acid, etc. Cases of lead-poisoning have been reported due to the cooking of food in vessels plated with tin containing lead. When a zinc rod is hung in a solution of lead salt, zinc liberates lead from the lead salt in a peculiar *crystalline* form called lead tree.

Uses of Lead.—It is used in making shots, bullets, plates for storage cells ; in preparing alloys ; in preparing lead chamber for H_2SO_4; evaporating pans, sinks, cisterns ; for roofing purposes ; the manufacture of pipes and sheathes for electric wires.

Alloys of Lead.—Common alloys of lead are :—*Typemetal* (Pb, 60%, Sb, 30%, Sn, 10%) : *Soft solder* (Pb and Sn) ; *Pewter* (Pb and Sn) ; *Linotype metal* (Pb 83, Sb, 14, Sn, 3).

Oxides of Lead.—Lead forms several oxides of which only three are important—

1. Lead monoxide (*Litharge, massicot*) ......PbO
2. Triplumbic tetroxide (*Red lead, minium*) ...Pb_3O_4
3. Lead dioxide or Lead peroxide ....PbO_2

Lead monoxide, PbO.—It exists in two varieties—(i) yellow powder commercially known as **massicot**; (ii) buff-coloured crystalline variety called **litharge** (which means *silverstone*).

Preparation.—It is prepared by heating lead, lead nitrate, or lead carbonate in air. It is obtained as a by-product in the cupellation process during the extraction of silver.

Litharge.—When massicot is heated, it melts. The molten mass on cooling solidifies giving the crystalline variety, called **litharge.**

Properties.—It is a yellow powder or a buff-coloured crystalline solid, insoluble in water. Lead monoxide dissolves in acids producing lead salts; it also dissolves in hot solution of NaOH or KOH giving the plumbite. Hence, it is an amphoteric oxide.

$$PbO + 2HCl = PbCl_2 + H_2O. \quad \| \quad PbO + 2NaOH = Na_2PbO_2 + H_2O.$$

Uses.—It is used in making flint glass; in glazing stoneware and earthenware articles; in the preparation of lead salts; and in making paints and varnishes.

Red lead, Pb_3O_4 (or 2PbO, PbO_2) occurs as **Minium.**

Manufacture.—Lead is heated in a current of air, whereby PbO is formed. PbO is removed and ground, any particles of unoxidised metal being, thereby flattened out, and thus easily removed by means of sieves. Finely powdered lead monoxide is now heated either on a reverberatory furnace or in a barrel-shaped vessel, open at both ends, in *excess of air* at 400°C for 48 hours. We get red lead. It is now washed and dried.

$$6Pb + 3O_2 = 6PbO \quad \| \quad 6PbO + O_2 = 2Pb_3O_4.$$

Properties.—It is a scarlet, crystalline powder, insol. in water. It decomposes when strongly heated giving lead monoxide $2Pb_3O_4 = 6PbO + O_2$. Dil. acids break up Pb_3O_4 into a mixture of PbO and PbO_2, the former now dissolves in dil. acids but not the latter. Thus we get a lead salt and PbO_2. Conc. HCl and conc. H_2SO_4 react with both PbO and PbO_2. Hence with conc. HCl, we get $PbCl_2$ and Cl_2, and with conc. H_2SO_4 we get $PbSO_4$ and O_2. Conc. HNO_3, however, dissolves *only PbO*. Hence we get $Pb(NO_3)_2$ and PbO_2.

$$Pb_3O_4 + 8HCl = 3PbCl_2 + Cl_2 + 4H_2O.$$
$$2Pb_3O_4 + 6H_2SO_4 = 6PbSO_4 + O_2 + 6H_2O.$$
$$Pb_3O_4 + 4HNO_3 = 2Pb(NO_3)_2 + PbO_2 + 2H_2O.$$

Uses.—It is used as a paint; in the manufacture of flint glass and in the manufacture of matches.

Lead dioxide, Lead peroxide, PbO_2.—It is prepared by the action of conc. HNO_3 on red lead, Pb_3O_4. Sol. is now diluted, filtered and PbO_2 washed and dried.

$$Pb_3O_4+4HNO_3=2Pb(NO_3)_2+PbO_2+2H_2O.$$

Properties.—It is a chocolate-brown amorphous powder. It is a powerful *oxidising* agent.

Uses.—It is used in the manufacture of matches, in storage cells and as an oxidising agent.

Lead hydroxide $Pb(OH)_2$—It can be obtained by the action of an alkali on any soluble salt of lead.

$$Pb(NO_3)_2+2NaOH=Pb(OH)_2+2NaNO_3$$

It is amphoteric dissolving both in acids and alkalis.

Properties.—It is a white solid, slightly soluble in water. The sol. turns red litmus-paper blue. It dissolves in acids. It *also* dissolves in alkalis, giving plumbites. When heated, it gives PbO.

Lead dichloride or Lead chloride, $PbCl_2$—It is obtained as a white ppt, when HCl, or a soluble chloride, is added to the solution of a lead salt. It may also be obtained by dissolving PbO or $PbCO_3$ in HCl.

$$Pb(NO_3)_2+2HCl=PbCl_2+2HNO_3.$$
$$PbO+2HCl=PbCl_2+H_2O.$$

Properties.—It dissolves in hot water, and when the solution is allowed to cool, it separates out in the form of white, lustrous *needle-shaped crystals*. It is very slightly soluble in cold water.

Lead nitrate $Pb(NO_3)_2$.—It is manufactured by dissolving lead, or litharge in hot, dilute nitric acid. The solution, on being evaporated, gives crystals of lead nitrate.

Properties.—It is a heavy, colourless, crystalline solid, soluble in water. When heated, it first melts and then decomposes into litharge, NO_2 and oxygen. *Basic lead nitrate*, $Pb(OH)NO_3$ is formed when lead nitrate solution is boiled with litharge.

Uses.—Lead nitrate is used in preparing (i) explosives, and (ii) NO_2 in the laboratory. It is preferred for the latter purpose, for it does not contain water of crystallisation.

White lead, $2PbCO_3\ Pb(OH)_2$ is a basic lead carbonate.

Manufacture.—Dutch Process. This is an old method, and though tedious, it gives white lead of excellent quality.

Pieces of lead are placed in earthenware pots having perforated shelves (or *ledge*) *near* the bottom, on which lead rests. Dilute acetic acid (*vinegar*) is taken in the pots. The pots are now placed, one above the other, with alternate layers of *spent tan-bark* or *horse dung*, inside a shed (fig. 112); and the whole stack is left as such for about 5 to 6 weeks. *Spent tan-bark* or *horse dung* undergoes fermentation; CO_2 is formed, and the heat generated volatilises acetic acid which attacks the lead giving basic lead acetate. Basic lead acetate is *now* decomposed by CO_2, producing basic lead carbonate (*white lead*), lead acetate and water.

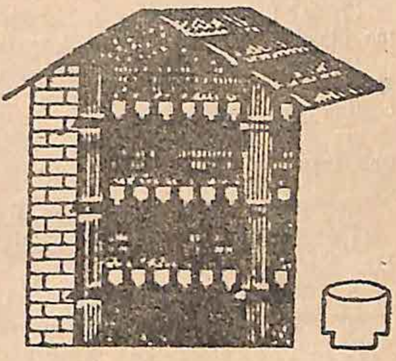


Fig. 112—Manufacture of white lead—Dutch Process.

When the lead is used up, the pots are taken down, the crust of white lead is detached, and is finely ground to separate it from any unchanged lead. It is now washed well with water and dried.

Uses.—White lead is extensively used as a pigment. Though it is poisonous and has this disadvantage that it turns black in presence of traces of H_2S in air, still it is preferred on account of its *opacity* and *covering power*.

Lead acetate. $(CH_3COO)_2Pb, 3H_2O$—It is also known as *sugar of lead* on account of its sweet taste. It is, however, poisonous. It is prepared by dissolving lead oxide or lead carbonate (avoiding excess) in hot dilute acetic acid, evaporating the solution and crystallising. When litharge is boiled with lead acetate a basic lead acetate is obtained which is used in medicine under the name of Goulard's lotion for treatment of sprain. Lead acetate is one of the few soluble salts of lead. It is used in the laboratory for the detection of H_2S and hence of sulphides which liberate the gas with HCl or dilute H_2SO_4.

Lead chromate, $PbCrO_4$ (chrome yellow).—It is the least soluble salt of lead. It is obtained as a bright yellow precipitate when a soluble chromate e.g., sodium or potassium chromate is added to lead acetate. $(CH_3COO)_2Pb + K_2CrO_4 = \downarrow PbCrO_4 + 2CH_3COOK$

It is used as a yellow pigment (Chrome yellow).

Detection of Lead

Dry test—*Charcoal test.*—Heat a compound of lead mixed with Na_2CO_3 on charcoal under the reducing *blow pipe* flame. A soft metallic bead of lead with *lemon-yellow* incrustation, is obtained. The lead is malleable and marks paper.

Flame test.—Pb-compounds, heated on asbestos fibre moistented with conc. HCl, impart a *lambent blue* colouration to the non-luminous Bunsen flame.

Wet test.—(1) Add dil. HCl to the solution of a lead salt. A *white* ppt. of $PbCl_2$ is obtained. Boil the precipitate with water. It dissolves. Cool, when needle-shaped crystals of $PbCl_2$ separate out.

(2) Add K_2CrO_4 sol. to the solution of a lead salt A yellow ppt. of lead chromate is obtained. The ppt. dissolves in mineral acids.

(3) Add KI solution to the solution of a lead salt. A yellow ppt. of PbI_2 is formed which dissolves in boiling water and precipitates out as *golden spangles* on cooling the solution.

(4) Pass H_2S through an acidulated solution of a lead salt. A black ppt. of PbS, soluble in hot HNO_3 of *moderate strength*. is obtained.

Exercise.

1. Name with formulae the oxides of lead and give their preparation and uses. How is lead extracted ?

2. What is white lead ? How is it made by the Dutch process ?

3. How will you proceed to detect the presence of lead if any in (*a*) *drinking water* and (*b*) *aluminium utensils* ? Lead is dissolved in HNO_3 and the sol. is evaporated, when crystals separate out. What are the crystals and what chemical changes take place when the crystals are heated ? *Cam, Jun. 1924.*

4. Give the formula of red lead. How would you prepare from this (*a*) lead peroxide, (*b*) crystals of lead nitrate. State the effect of heat on each compounds. Give equations. What is the action of HCl on *(a)* red lead, *(b)* lead nitrate ? *C. U. I. Sc., 1959.*

CHAPTER XXXIII

IRON

Symbol, Fe At. wt., 56. At. no., 26.

History.—Iron has been known from pre-historic time.

Occurrence.—Iron does not occur in the 'free' state. Small quantities of native iron have been found in bodies called meteorites which do not actually belong to this earth but occasionally reach its surface from the outer space. Iron occurs—

(1) as **Oxide.**—(*a*) Magnetic iron ore or Magnetite, Fe_3O_4 ; and (*b*) Red haematite, or *Specular iron ore*, Fe_2O_3.

(2) as **Hydrated Oxide.**—Brown haematite or Limonite, $2Fe_2O_3\,3H_2O$.

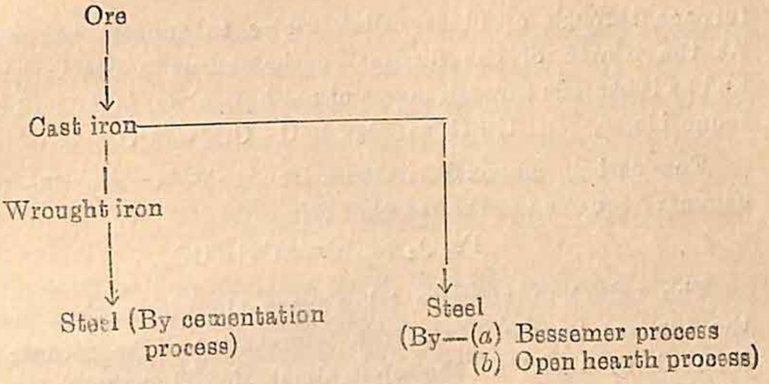
(3) as **Carbonate.**—Spathic iron ore, *Spathose* or *Siderite*, $FeCO_3$.

(4) as **Sulphide.**—Iron pyrites, Fe_2S_3 and Marcasite, FeS_2.

Iron pyrites, on account of its high sulphur content, is not used as an ore for the extraction of iron, but is more profitably used in the manufacture of SO_2 and H_2SO_4.

The Metallurgy of Iron

There are three varieties of commercial iron, *viz.*—*Cast iron*, *wrought iron* and *steel*. These are made in the following order—



Manufacture of cast iron

It consists of two steps—

(1) *Preliminary roasting or calcination*—The ore, particularly if it is a carbonate or hydrated ferric oxide (brown haematite), is calcined in order to drive out moisture and carbon dioxide and also to convert any ferrous material into ferric state.

(2) *Reduction or Smelting*—The calcined ore mixed with limestone and coke is smelted in a blast furnace.

The Blast Furnace : The blast furnace consists of a cylindrical structure, the outside of which is made of steel plates revetted together and the inside is lined with fire bricks. It is about 50-120 ft. high. It broadens from the top and at its broadest part (boshes) which is about two-thirds of its way to the ground it is about 16—24ft. wide. Below the boshes, the furnace narrows down and at its bases is the hearth where iron and slag collect. The action is started by burning a quantity of wood on the hearth of the furnace. The furnace is gradually filled with the calcined ore, limestone and coke in alternate layers which are fed intermittently into it through a cup-and-core arrangement by lowering the cone without excessive escape of the gas from inside, (fig. 113). At a level just above the hearth, pre-heated air at about 600°C is admitted into the

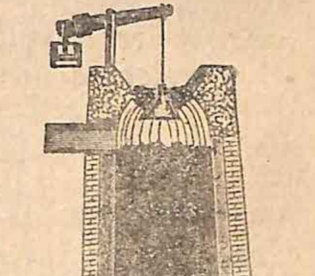


Fig. 113—Blast furnace

furnace through openings called *tuyers* to support the combustion. At the hearth of the furnace, carbon burns to form carbon dioxide and as it ascends through layers of red-hot coke it is reduced to carbon monoxide. $C + O_2 = CO_2$ $C + CO_2 = 2CO$.

The carbon monoxide reduces iron oxide to metallic iron; the summary equation of the reaction being

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2.$$

The reduction actually takes place stepwise in the upper part of the furnace (see fig. 114). The temperature of the furnace increases from about 450°C at the top to about 1500°C at the base. The reduced iron, still solid, settles down and at the bosh at a temperature of about 1200°C, it melts in contact with coke having partly absorbed it. The iron by absorbing carbon is turned into cast iron. Its melting point is greatly lowered by the addition of carbon. At the temperature of the furnace limestone decomposes into lime and CO_2

$$CaCO_3 = CaO + CO_2.$$

The lime combines with the silica of the ore to form calcium silicate (*slag*).

$$CaO + SiO_2 = CaSiO_3$$

The molten iron drips into the hearth covered with a layer of lighter molten slag. The slag and the cast iron are discharged at intervals through their respective tap holes which are plugged during the rest of time with clay.

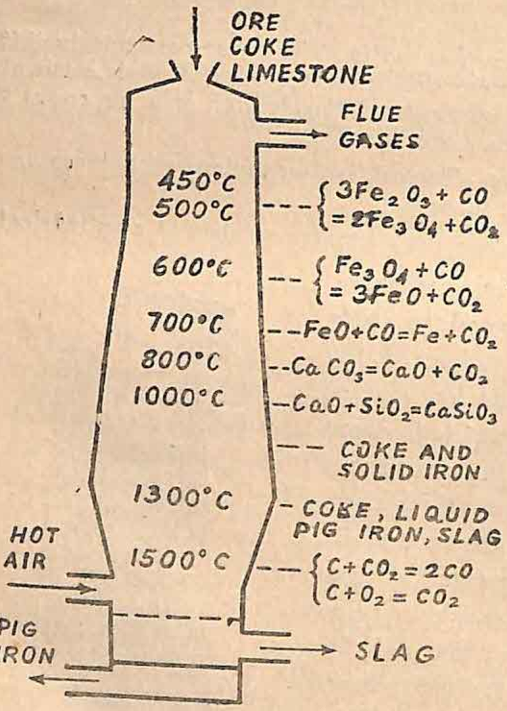


Fig. 114—The stepwise reduction of ore in the blast furnace.

The waste gases escaping through a flue near the throat of the furnace contain sufficient CO (up to 25%) which is burnt in towers called Cowper stoves packed with chequered brick-works. Cowper stoves work in pairs. While one stove is being heated up, dust free air which is to be blown into the blast furnace later is passed through the other which has been already heated up in like manner.

In modern practice, oxygen is being used instead of air. In that case, oxygen need not be pre-heated thus eliminating clumsy Cowper stoves.

Cast iron—The iron obtained from the blast furnace, is cast into *pigs* in steel moulds. The product **pig iron** contains 2·5% of carbon together with silicon, phosphorus, sulphur, manganese etc. in varying amounts. The pig iron is brittle and cannot be worked by rolling and hammering. But pig iron can be remelted and cast into different useful forms by means of moulds. Hence the name **cast iron.** Cast iron is particularly suitable for casting. It has a lower melting point than steel or wrought iron and it expands on solidification. Hence it gives a good reproduction of the mould. On account of the brittleness, it is only suitable for ornamental iron work and for articles not generally exposed to great strain.

A large part of cast iron is converted into steel and a small part into wrought iron.

Varieties of Iron.—There are *three* forms of iron, *viz Cast iron, Steel* and *Wrought iron*, the nature of which depends upon the amount of impurities, especially carbon, present in iron. Thus *Cast iron* containing the highest proportion of carbon is the most impure form of commercial iron ; *Wrought iron* containing the minimum amount of carbon is taken as the purest form of commercial iron ; while *Steel* lies intermediate between the two.

There are again two varieties of cast iron :—*White cast iron,* which contain *major portion* of Carbon in the combined form ; and *Grey cast iron* which contains *major portion* of carbon distributed throughout the mass in the form of minute crystals of graphite. Hence the gley colour. There are *also* different varieties of steel, *viz*, **Mild Steel, Alloy Steel,** etc.

Cast iron	*Steel*	*Wrought iron or Malleable or Soft iron*
2—5% of carbon : also Si, Mn, P, S, etc.	·25—1·5% of Carbon.	·12 – ·25% of Carbon.

Wrought iron.—Wrought iron is the purest variety of commercial iron containing 0·12% to 0·25% of carbon with still smaller quantity of other impurities. It is made by melting cast iron on the bed of a reverberatory furnace lined with ferric oxide. The oxygen of the ferric oxide oxidises the carbon present in cast iron into carbon monoxide.

$$Fe_2O_3 + 3C = 2Fe + 3CO$$

The other impurities sulphur, phosphorus, silicon, manganese etc. also undergo oxidation and either escape as gases or form slags with the lining. As the impurities are removed, the melting point of iron rises and the mass becomes pasty. It is then worked up into balls (blooms) and hammered to squeeze out the slag.

Wrought iron is a strong, tough metal which can be readily welded and forged. On account of these properties and its comparative freedom from corrosion, it was used at one time extensively for making chains, wires and similar articles. Now it has been largely replaced by mild steel.

Manufacture of Steel

From Wrought Iron : Cementation Process—This process is now obsolete. It is the oldest method of steel making once largely used in India and Damascus.

Bars of wrought iron are packed with powdered charcoal in sealed firebrick boxes and heated to redness for several days. The bars gradually absorb carbon and pass into steel without melting. The steel is called blister steel due to blistered surface. The blister steel is melted in plumbago crucibles to form crucible steel.

(*a*) **From Cast Iron : Bessemer process**—In this process a converter is used for steel making. The converter is an egg-shaped vessel lined inside with silica bricks and mounted on trunnions by means of which it can be tilted. There is an air chamber at the base connected with an iron pipe from which air can be blown through holes in the lining (fig. 115).

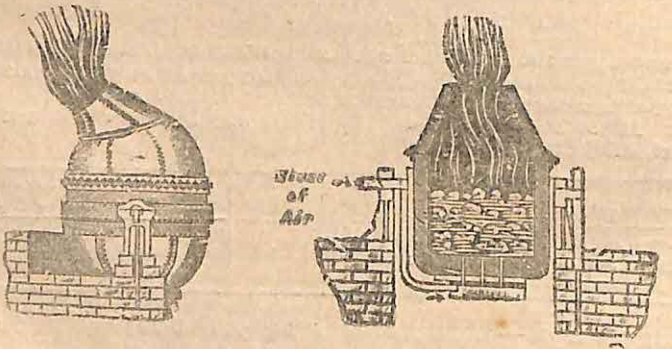


Fig. 115—Manufacture of steel—Bessemer process

The converter is filled with several tons of molten cast iron. Air is forced in through opening at the bottom of the converter which oxidises the impurities. In less than 20 minutes, the impurities are all burnt out, either escaping as gases or forming slags. Carbon is oxidised to carbon monoxide which burns with a large flame at the mouth of the converter. When all the carbon is burnt out, the flame sinks. Now the blast is stopped and requisite quantity of spiegeleisen —a ferromanganese containing the required quantity of carbon is added. The steel is now poured out and cast into moulds.

If the converter has a lining of silica (*Acid Bessemer process*), phosphorus if present in pig iron, cannot be eliminated. In such case, the lining in made of calcined dolomite, $MgCO_3$, $CaCO_3$ (basic lining) and some lime is added with the charge. P_2O_5 formed by the combustion of phosphorus combines with lime and magnesia to form basic slags (used as fertiliser). This process invented by the English scientists S. G. Thomas and P. C. Gilchrist is known as *Basic Bessemer Process*.

(*b*) **Siemen Martin open hearth process.**—Molten cast iron is run into the bed of an open hearth furnace (fig. 116) which is lined either with silica or if phosphorus is present in cast iron, with lime and magnesia. The open hearth furnace is heated by producer gas and works on the principle of heat regeneration. Heat produced in the furnace is utilised to pre-heat the air and the producer gas used in the furnace by means of two sets of heat interchangers. While one set is being heated up by the furnace gases, producer gas and air are heated up by passing through the other set. The arrangement is reversed after some time.

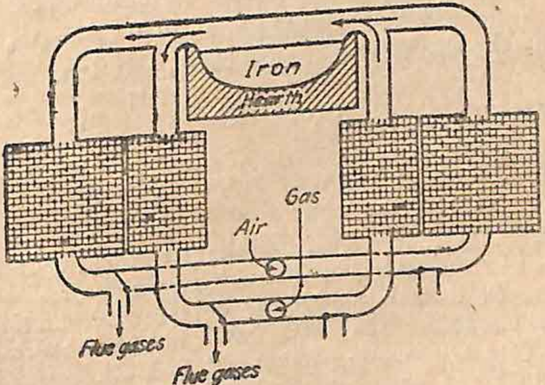


Fig. 116—Manufacture of steel—Open hearth process

In the open hearth furnece, cast iron is melted with scrap steel and heamatite iron ore. The impurities are burnt out partly by air and partly by the oxygen of the ore, passing into slag or escaping as gases. Requisite amount of carbon in the form of spiegeleisen is added to the decarbonised iron to convert it into steel which is then cast into ingots.

Advantages of open hearth process.—Because an external heat source (producer gas) is used, the process can be continued as long as desired (10 hours as against 20 minutes in the Bessemer process). This ensures a more thorough removal of impurities than is possible in the Bessemer process and hence steel obtained is of a better quality.

Heat treatment of Steel—The mechanical properties of steel can be greatly altered by heat treatment i.e. heating and cooling under definite conditions. If steel is heated to redness and then quenched suddenly in cold water, it becomes hard and brittle. This process is called *hardening of steel.* When the hardened steel is reheated to various temperatures (lower than before) and then cooled slowly, it becomes soft and elastic. This process is called *annealing of steel.* The two processes together are known as *tempering.*

Alloy Steel—It is found that the presence of other metals imparts new and valuable properties to steel. Manganese steel (13-14%) is very hard and is used for making grinding and crushing machines. Stainless steel (11% Cr and 8% Ni) contains chromium. Nickel steel has a low thermal co-efficient. Tungsten and Molybdenum steels are used for high-speed cutting tools.

Pure Iron—Chemically pure iron may be obtained either by heating pure Fe_2O_3 in a current of pure H_2 at 1000°C ($Fe_2O_3 + 3H_2 = 2Fe + 3H_2O$) or by the electrolysis of pure $FeCl_3$ solution.

Properties

Physical.—Pure iron is a white metal, highly tenacious, ductile and malleable. Its sp. gr. is 7·85. It melts at 1533°C and boils in the electric furnace. Iron is magnetic.

Chemical.—(1) *Action of air.*—It is not acted upon by dry air at the ordinary temperature, but it rusts in moist air. When strongly heated, it burns in oxygen producing Fe_3O_4. (2) *Action of water*—Pure iron does not react with pure water, but red-hot iron decomposes steam. (3) *Action of acids.*—With HCl and dil. H_2SO_4, iron gives hydrogen and ferrous salts ; with dil. HNO_3 it gives ferrous nitrate and ammonium nitrate whereas ferric nitrate and NO_2 are produced with conc. HNO_3.

$$4Fe + 10HNO_3 = 4Fe(NO_3)_2 + 3H_2O + NH_4NO_3$$

$$Fe + 6HNO_3 = Fe(NO_3)_3 + 3H_2O + 3NO_2$$

Highly conc. HNO_3 (sp. gr. 1·50) does not dissolve iron. Iron is then said to be in the *passive state*. This *passivity* is said to be due to the deposit of a thin layer of iron oxide on the surface. (4) *Action of alkalis.*—Alkalis have no action on iron. (5) Heated in chlorine, iron gives ferric chloride, $FeCl_3$. It also combines directly with bromine, iodine and sulphur. (6) Iron absorbs CO at 120°C .to from iron carbonyl, $Fe(CO)_5$. (7) Iron can liberate copper from the solution of copper salts.

Properties of Cast Iron, Steel and Wrought Iron

Properties	**Cast Iron**	**Steel**	**Wrought Iron**
1. *Amount of Carbon*	2 to 5%	·25 to 1·5%	·12 to ·25%
2. *Melting point*	1200°C	1300°C—1400°C	1500°C
3. *Brittleness* or *Malleability*	brittle	malleable and brittle	malleable
4. *Hardness*	hard	hard and soft	soft
5. *Structure*	crystalline	crystalline	fibrous
6. *Tempering*	cannot be tempered.	can be tempered,	cannot be tempered
7. *Welding*	cannot be welded	can be welded	can be welded
8. *Magnetisation*	cannot be permanently magnetised	can be permanently magnetised	cannot be permanently magnetised
Uses of Cast Iron, Steel and Wrought Iron	For casting articles and for the manufacture of Steel and Wrought iron	In the manufacture of railway lines, locomotives, joists, cranes, etc., in the manufacture of war implements, surgical instruments, cutlery, etc; preparing artificial magnets watch springs etc.	In the preparation of *cores* of electro-magnates; piano-wires; and wire-netting.

Compounds of Iron.—Iron forms two series of compounds—compounds of divalent and trivalent iron designated as ous and ic respectively.

Oxides of Iron: **Ferrous oxide, FeO**—It is a black solid insoluble in water. It may be prepared by passing hydrogen over Fe_2O_3 at 300°C $Fe_2O_3 + H_2 = 2FeO + H_2O$.

It is used for imparting green colour to glass.

Ferric Oxide, Fe_2O_3—It occurs as red haematite. It is prepared commercially by heating ferrous sulphate.

$$2FeSO_4 = Fe_2O_3 + SO_2 + SO_3$$

It is a deep red solid, insoluble in water. It is used under the name rouge as jewellers' polish and a paint under various trade name, e g., venetian red.

Besides these two oxides, there is one more—magnetic oxide of iron, Fe_3O_4 which occurs as a mineral magnetite or **lodestone.**

Ferrous Chloride, $FeCl_2$—It may be prepared by the action of dil. HCl on iron wire in the absence of air. In the hydrated form ($FeCl_2, 4H_2O$), it is obtained by dissolving iron or iron sulphide in dil. HCl.

Anhydrous $FeCl_2$ is a colourless crystalline solid soluble in water. Hydrated salt is, however, green in colour. It is oxidised by chlorine into ferric chloride. $2FeCl_2 + Cl_2 = 2FeCl_3$

Ferric Chloride, $FeCl_3$—Anhydrous ferric chloride is prepared by passing chlorine over heated iron wire in a hard glass tube fitted with a bottle. Ferric chloride collects inside the bottle.

Anhydrous $FeCl_3$ is black ; hydrated salt is, however, green. $FeCl_3$ is a deliquescent crystalline substance. It is styptic, i.e. has the power to coagulate blood and stop bleeding. It is reduced by nascent hydrogen, H_2S etc. into ferrous chloride.

$$2FeCl_3 + H_2S = 2FeCl_2 + 2HCl + S.$$

$FeCl_3$ is used as styptic in medicine and as a laboratory reagent.

Ferrous Sulphate (Green vitriol) $FeSO_4, 7H_2O$—

Preparation.—It is obtained by treating ferrous sulphide or ferrous carbonate with dilute H_2SO_4.

Manufacture.—Heaps of Marcasite, FeS_2 are exposed to the action of air and moisture and thus allowed to undergo *slow* oxidation. Marcasite is oxidised into ferrous sulphate. The resultant mass is treated with water, when a solution of ferrous sulphate with free H_2SO_4 is obtained. The free acid is converted into *more* ferrous sulphate by adding scrap iron to the solution. It is allowed to stand, and the solution is taken off and evaporated.

$$2FeS_2 + 2H_2O + 7O_2 = 2FeSO_4 + 2H_2SO_4 \parallel H_2SO_4 + Fe = FeSO_4 + H_2$$

Properties.—It is a pale-green, crystalline solid, containing seven molecules of water of crystallisation. It **effloresces** on exposure to the air. It gradually turns brown owing to oxidation into the ferric compound by the atmospheric oxygen. When **heated,** the monohydrate, $FeSO_4, H_2O$ is first formed, and this, on heating at 300°C in absence of air, gives the *anhydrous* salt which is *white* in colour. At a red heat, in *vacuum* at 140°C, it decomposes into $Fe_2O_3 + SO_3 + SO_2$. $2FeSO_4 = Fe_2O_3 + SO_2 + SO_3$. It is soluble in water and the solution absorbs NO.

Uses.—It is used in the preparation of writing-ink ; in the manufacture of *rouge* ; in dyeing industry ; and in medicine.

Ferric Sulphate $Fe_2(SO_4)_3$—It may be obtained by dissolving ferric oxide in sulphuric acid or oxidising ferrous sulphate in presence of conc. H_2SO_4 by HNO_3. $Fe_2O_3 + 3H_2SO_4 = Fe_2(SO_4)_3 + 3H_2O$.

It forms ferric ammonium alum (iron alum) with ammonium sulphate. Under the action of ammonia or alkalis, we get a ppt. of brown ferric hydroxide insoluble in water or excess of the reagent.

Ferrous Sulphide, FeS—It is prepared by heating iron filings and sulphur together. $Fe + S = FeS$

It is a black mass having metallic lusture. It is insoluble in water. When treated with dil. HCl or dil. H_2SO_4, H_2S is liberated. It is used in laboratory Kipp's for the generation of H_2S gas.

Rusting of Iron

When a piece of Iron is exposed to ordinary moist air, it is found to be covered with a loose, non-coherent, easily detachable, brown coating called rust. The process is called rusting,, and it is a case of *slow combustion*.

What is rust ?—Partington suggests that rust is chiefly hydrated Ferric oxide having the formula, $2Fe_2O_3 . 3H_2O$. Some Chemists, however, think that the composition of rust is not so simple, and it contains Ferrous carbonate and hydrated Ferrous oxide as well, the amounts of which depend upon the age of the rust. If the rust has been long exposed to the air, the amounts of the Ferrous compounds become very small, and ultimately, hydrated Ferric oxide predominates.

Theory of Rusting—There are three theories :—(1) Iron rusts as result of oxidation of the metal through the intermediate formation of $FeCO_3$.

$Fe + H_2O + CO_2 = FeCO_3 + H_2$ ‖ $4FeCO_3 + 6H_2O + O_2 = 4Fe(OH)_3 + 4CO_2$.

(2) Some chemists suggest that CO_2 is not essential. Rusting takes place through the action of H_2O_2. $Fe + O_2 + H_2O = FeO + H_2O_2$,

$$2FeO + H_2O_2 = Fe_2O_3 + H_2O.$$

It must be pointed out that there is no direct evidence of the formation of H_2O_2. The theory has been based on the fact that substances which *destroy* H_2O_2 retard rusting. Similarly, *alkaline waters* which remove CO_2 also retard rusting.

(3) Since *pure Iron does not appreciably rust* in moist air, it has been suggested that a kind of tiny voltaic cell is set up between the impurities of Iron and iron itself in contact with water, with the result that iron rusts. This is the Electrolytic theory of rusting.

Prevention—Rusting may be *put off*—(1) by covering the metal with paints (especially Al paint, red oxide), coal tar, pitch etc. : (2) by blowing steam over the red-hot metal so that a layer of Fe_3O_4 is deposited on the surface ; (3) also by *galvanising* and *tinning*.

Rusting is a kind of slow combustion—Rusting is principally due to combination of iron with the Oxygen of air. It is, therefore, a case of oxidation. We know that when Iron wire is strongly heated in Oxygen by means of electric current or when a piece of strongly heated Iron wire is inserted into a jar of Oxygen, it burns with scintillation giving Fe_3O_4, which is an oxide of iron with this difference that, unlike rusting, it is attended with evolution of much heat and light. Now, in a general sense, any chemical union attended with the evolution of heat and light is called combustion. Hence, when Iron burns in Oxygen with scintillation, it undergoes combustion.

There are cases, however, where combustion takes place with evolution of heat but little or no light as the slow oxidation of sugar in our blood by the air we inhale which produces some heat, but no light. Hence rusting is a kind of slow combustion.

Detection of Iron

1. **Dry test.**—(*a*) Compounds of iron heated with Na_2CO_3 on charcoal under the reducing blow-pipe flame leave a black powder which is attracted by a magnet.

(*b*) When salts of iron are heated on a clean borax-bead, the bead is coloured *yellow* in the oxidising flame, and *bottle green* in the reducing flame.

Exercise

1. Name the principal ores of Iron. How is the metal extracted from these? State the composition, properties and uses of the three forms of the metal. What is the cause of the different properties of Cast iron, Wrought iron and Steel? How is the purest form of Iron obtained?

2. What is Steel? Describe Bessemer and Open-hearth processes for the manufacture of Steel.

3. Describe the preparation of Green vitriol from ferric oxide and *vice versa.*

4. What is the difference in chemical composition and physical properties between Cast iron, Wrought iron and Steel? State their respective uses. Describe two important methods by which Steel is prepared from Cast iron.

5. Name the principal ores of Iron. Give outlines of the extraction of cast iron from the ores. Give equations to represent the reactions involved in this extraction.
Cal. Pre-U., 1963.

6. Name and write the formulae of the important ores from which the metal Iron is obtained. Give in outline the method for the extraction of the metal from its ore.
Cal. Pre-U., 1965.

CHAPTER XXXIV

NICKEL

Symbol, Ni. At. wt., 58·61 At. No., 28

Occurrence.—Nickel is found in the free state in meteorites. The chief ores of Ni from which the metal is extracted are pentlandite (Fe Ni) S found at Sudbury near Ontario in Canada (Sudbury ore) and Garnierite. a double silicate of magnesium and nickel (NiMg) SiO_3, nH_2O.

Extraction of Nickel from Sulphide Ore (Sudbury Ore)

The Sudbury ore contains copper pyrities, $CuFeS_2$ together with NiS (a mixture of FeS_2, FeS, Cu_2S and NiS).

It is first concentrated by oil floatation process. The concentrated ore is first of all roasted to remove some of the sulphur.

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2$$
$$2NiS + 3O_2 = 2NiO + 2SO_2$$
$$Cu_2S + 2O_2 = 2CuO + SO_2$$

The roated ore is then smelted with quartz, coke and limestone in a small blast furnace when much of the iron is oxidised and passes into the slag as ferrous calcium silicate. The product is poured into a Bessemer converter with a basic lining and air is blown in to oxidise iron and sulphur giving a *matte* containing 50% Ni, 30% Cu and 20% Sulphur.

Reduction of Matte by Mond's Process

In the Mond's process, the matte is roasted yielding oxides of nickel and copper. The roasted matte is treated with dilute sulphuric acid which dissolves out the copper oxide leaving nickel oxide undissolved. Nickel oxide is now reduced by water gas to metallic nickel.

$$NiO + H_2 = Ni + H_2O.$$

The metal still contains some copper. It is refined by passing CO over it at 60°C whereby volatile nickel carbonyl is produced.

$$Ni + 4CO = Ni(CO)_4.$$

Nickel Carbonyl is passed over nickel shot heated to 180°C where it decomposes forming Ni and CO. $Ni(CO)_4 = Ni + 4CO$.

Compounds of nickel

Four oxides of nickel are known of which nickelous oxide is the most important.

Nickelous oxide (Nickel monoxide), NiO is obtained by carefully heating the hydroxide or the carbonate. $NiCO_3 = NiO + CO_2$.

It is a green solid insoluble in water. It is reduced to nickel by hydrogen or carbon monoxide.

Nickel Chloride, $NiCl_2$ can be prepared in the anhydrous state by the action of chlorine on nickel. In the hydrated state ($NiCl_2, 6H_2O$) it is obtained by dissolving nickel oxide or the carbonate in HCl, evaporating and crystallising. The anhydrous salt is golden yellow in colour and the hydrated salt green. It is soluble in water. Anhydrous salt absorbs ammonia giving the compound, $NiCl_2, 6NH_3$.

Nickel Carbonate, $NiCO_3, 6H_2O$.—It may be obtained by adding nickel sulphate solution to a solution of sodium bicarbonate in water saturated with CO_2. With Na_2CO_3 solution, nickel salt solution gives a ppt. of the *basic carbonate of nickel.*

Properties.—It is a *green* solid insoluble in water. It dissolves in acids giving nickel salts with the evolution of CO_2.

Nickel Sulphate, $NiSO_4, 7H_2O$—It may be prepared by dissolving nickel, its oxide, hydroxide or carbonate in dil. H_2SO_4 and evaporating the solution to crystallisation, when crystals of $NiSO_4, 7H_2O$ separate out. It is a green crystalline solid soluble in water.

Nickel Carbonyl, $Ni(CO)_4$.—It is prepared by passing carbon monoxide (usually under increased pressure) over *reduced* nickel at 30°C.

Properties.—It is a colourless, strongly refracting liquid freezing at $-25°C$ and boiling at 43·2°C. The vapour has the *normal* Mol. wt. It decomposes completely under atmospheric pressure at about 180°C. It is insoluble in water but slowly liberates hydrogen from acids. It is decomposed by the halogens. $Ni(CO)_4 + Cl_2 = NiCl_2 + 4CO$.

Nickel-plating.—For details, see fig. 104. Use nickel ammonium sulphate sol. *saturated* at 20°—25°C and suspend a polished strip of pure nickel from the anode, and the article to be nickel-plated from the cathode.

Detection of Nickel

Dry Test.—(1) *Charcoal test.*—Compounds of nickel mixed with Na_2CO_3 and heated on charcoal under the *reducing* blow-pipe flame, yield a black magnetic mass.

(2) *Borax-bead test.*—Compds. of nickel, when heated on a borax bead, colour the bead *reddish-brown* in the oxidising flame, and *grey* and *opaque* in the reducing flame.

Wet Test.—(1) Nickel salt sol. treated with $(NH_4)_2S$ gives a black ppt. of NiS insoluble in moderately conc. HCl but soluble in *aqua regia*, and in conc. HCl mixed with $KClO_3$.

(2) Nickel salt sol. treated with $NH_4(OH)$ gives a *greenish* ppt. The ppt. dissolves *in excess* of $NH_4(OH$ giving a *deep blue* solution.

(3) Nickel salt sol. treated with KCN sol. gives a green ppt. of $Ni(CN)_2$ soluble in excess of KCN sol. forming $K_2Ni(CN)_4$. The ppt. turns *black* on being warmed with NaOH and Br-water.

(4) Nickel salt sol. treated with Na-acetate and acetic acid and then with **dimethyl glyoxime** gives a *red* ppt. of nickel dimethyl glyoxime.

Separation of Co from Ni by Dimethyl glyoxime.

Take the mixture of Ni-salt and Co-salt sol. and add Na-acetate to it. Heat the sol. almost to boiling and add excess of alcoholic sol. of *dimethyl glyoxime*. Now add excess of $(NH_4)OH$, stir and warm the sol. Red ppt. of Ni-dimethyl glyoxime is formed. Filter. Evaporate the filtrate containing the cobalt salt to dryness, and try *borax-bead* test for cobalt.

Exercise.

1. What are the important ores of nickel? How is the metal extracted from its ores? State its properties and uses.

2. What are the names of the following compounds and how they are prepared? $Ni(OH)_2$; $NiSO_4, 7H_2O$; NiS; $Ni(NO_3)_2, 6H_2O$ and $NiCO_3, 6H_2O$.

THE CHEMISTRY OF CARBON COMPOUNDS

(ORGANIC CHEMISTRY)

CHAPTER XXXV

INTRODUCTION

Definition and Scope of Organic Chemistry :

Since the term 'Organic' was first coined to denote compounds obtained from the living world, i.e. from plants and animals, its meaning has greatly changed. Now it is used with respect to all carbon compounds, no matter whether they are produced in the bodies of living organism or are products of pure laboratory synthesis. At one time there was a strong belief among the scientists that formation of an organic compound could only occur in living cells through the intervention of a vital force (*theory of vital force*) and as such it was completely beyond the power of man to prepare it artificially.

A German scientist, Friedrich Wohler in 1828 first prepared urea (an organic substance of animal metabolism which is excreted with urine) by reacting ammonia with cyanic acid. Wohler's experiment by disproving the theory of vital force gave an impetus to the growth of organic chemistry which ever since became one of the most progressive branches of science. Theoretically, there remained little justification for drawing a sharp line of demarcation between organic and inorganic compounds.

Organic Chemistry is now simply defined as the Chemistry of Carbon Compounds :

Carbon monoxide, carbon dioxide, metallic carbonates and some other simple organic compounds are dealt in Inorganic chemistry partly on account of their extensive occurrence in the mineral world and partly to show the relation of carbon with other elements in the periodic table.

There are, however, several cogent reasons which have stood in the way of merging the compounds of carbon with those of other elements in a single book of chemistry. Some of these reasons are enumerated below.

(1) Very large number of organic compounds amounting to several lacs which many times outnumber those of other elements put together, is the major obstacle in the way.

(2) Moreover organic compounds are far more complex having large molecular formulae. Starch, for example, is represented by the molecular formula $C_{1200}\ H_{2000}\ O_{1000}$. In contrast, molecular formulae of inorganic compounds are very simple—H_2O, HCl, H_2SO_4 etc.

(3) The molecular formula of an organic compounds does not characterise it completely, for the same molecular formula may stand for more than one, sometimes several hundreds or more compounds. This is unique and is not met with anywhere among inorganic compounds. H_2SO_4 always stands for sulphuric acid and for no other compounds.

The different compounds, having the same molecular formula is known as *isomers* and the phenomenon is called *isomerism*. For example, there are two compounds with the same molecular formula, C_2H_6O. One of them, ethyl alcohol is a liquid and the other, dimethyl ether, a gas of altogether different properties. The phenomenon of isomerism is due to difference in the arrangement of the same atoms within the molecule. Thus, the molecular formula is only of minor importance in the study of an organic compound. We must know the arrangement of the atoms within the molecule or in other words, its structural formula which alone determines it completely.

(4) Organic compounds are non-polar, the constituent atoms in an organic molecule being bound by covalent bonds. Inorganic compounds, on the other hand are polar with constituent atoms joined by electrovalency. Inorganic compounds are electrolytes, but organic compounds are non-electrolytes.

(5) Covalent bonds are difficult to break; hence organic reactions which are, as a rule, non-ionic are slow to take place in contrast to inorganic reactions, which being ionic take place almost instanttaneously.

Structural Formula and Classification

Structural formula : We have seen how important it is to know the structural formula of an organic compound for its rational study. So it is the foremost as well as the most difficult, nevertheless, the most interesting part of the business of an organic chemist engaged in the study of an unknown organic compounds to determine fully its structure. Once this is done, its ultimate synthesis is only a matter of time.

To find the structural formula of a substance, one must first of all determine its molecular formula which is again obtained by way of its empirical formula. The different steps may be briefly outlined as follows :

(1) First, the unknown organic compound is purified by processes such as crystallisation, distillation etc, already discussed in the earlier part of this book.

(2) When the compound is obtained in the pure state, it is subjected to qualitative and quantitative analysis. By means of the former, the elements present in the compound are found out and by means of the latter their percentages are estimated. The percentage composition of a substance enables its empirical formula to be calculated. The steps in the calculation are as follows :

(*i*) Divide the percentage weights of different elements by their respective at. wts.

(*ii*) Divide the quotients (if they are not whole numbers) by a suitable number (usually the lowest quotient or a submultiple of it) in order to convert them into integeres. The integers obtained, give the ratio of the different atoms present in the molecule or in other words its empirical formula.

Illustration.—Find out the formula of ether having the following percentage composition · C=64·86%, H=13·51%, O=21·62%.

Application of the above Rule :

	Percentage weight	$\frac{\text{Percentage wt.}}{\text{Atomic wt.}}$	Ratio of atoms	Dividing each by the lowest number 1·35 we get	Ratio in whole number
Carbon—	64·86	$\frac{64{\cdot}86}{12}$	5·4		4
Hydrogen—	13 51	$\frac{13{\cdot}51}{1}$	13·51		10
Oxygen—	21·62	$\frac{21{\cdot}62}{16}$	1·35		1

Thus, we get the ratio of the number of atoms of carbon : hydrogen : oxygen=4 : 10 : 1. A molecule of *ether*, therefore contains the elements of carbon, hydrogen and oxygen in that ratio, and its empirical formula is $(C_4H_{10}O)$.

Molecular formula gives the exact number of different atoms in the molecule of a substance. It is an exact multiple of the empirical formula.

For example, the empirical formula of glucose is CH_2O. Its molecular formula is $(CH_2O)n$, where n=integer.

To find n we must know the mol. wt. of the substance which if volatile, can be determined by Victor Meyer's method. Other methods are available for the determination of mol. wts. of non-volatile substances. From the value of the mol. wt., n can be found out.

For example, the mol. wt. of glucose is 180. Therefore

$$(CH_2O)n = 180$$

or, $(12+2+16)n = 180$ or, $30n = 180$ or $n = 6$.

∴ The molecular formula of glucose is $(CH_2O)_6$ or $C_6H_{12}O_6$.

The determination of the structural formula from molecular formula is a much more ardous task. Kekule', a German scientist first devised a method for finding the structural formula of a compound. He put forward a theory known as the *theory of carbon linkages* According to this theory, the carbon atom was given a fixed combining capacity (valency) of four which were represented symbolically by hypens (or hands) proceeding from the carbon atom. The four valencies were shown in the structural formulae of Kekule', as lying in one plane. It was later shown by Van't Hoff and Le Bel that the four valencies of carbon were actually directed in space making equal angles (109°28′) with one another. This would be achieved if we put the carbon atom at the centre of an imaginary regular tetrahedron with its four valencies directed towords its four corners. (fig. 117*a* and 117*b*).

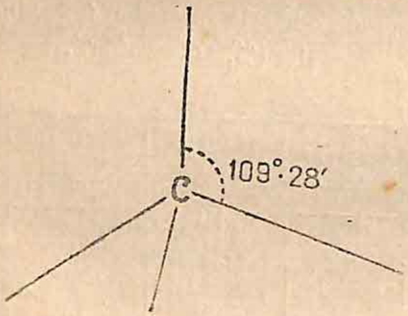


Fig. 117(*a*)—Normal direction of carbon valencies.

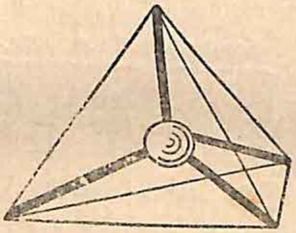
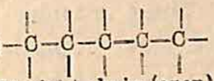
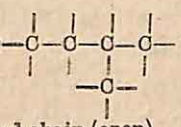


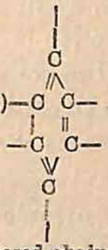
Fig 117(*b*)—Tetrahedral distribution of carbon valencies.

Kekule', moreover, assumed in his theory that the carbon atoms possess unlimited power of combining among themselves forming

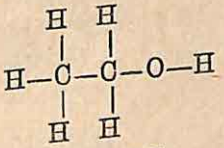
(1) open chains which might be (*a*) straight or (*b*) branched or (2) closed chains as shown below.

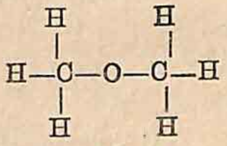
1. (a)

Straight chain (open)

1. (b)

Branched chain (open)

(2)

Closed chain

An organic compound contains one or more such chains to which atoms of hydrogen oxygen, nitrogen etc., are attached by their respective hands so that the hands of every atom in the molecule including those of carbon become fully engaged. We have seen that the molecular formula, C_2H_6O may stand for two compounds ethyl alcohol and dimethyl ether. Let us see how Kekule's theory enables us to find their respective structural formula. Now taking the valencies of carbon to be four, that of oxygen two and hydrogen one, the atoms contained in the molecule, C_2H_6O can be arranged only in two ways.

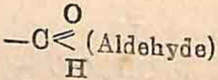
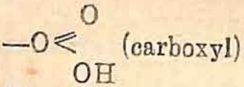
(I)

$$H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-O-H$$
or, $CH_3.CH_2OH$

(2)

$$H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-O-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-H$$
or, $CH_3.O.CH_3$

We find that the properties of ethyl alcohol can be better explained by structural formula (1) than by (2) for example, when ethyl alcohol is treated with metallic sodium, only one out of the six hydrogen atoms is displaced. This shows that one of the hydrogen atoms must be differently linked from the rest so that it is expelled to the exclusion of the other. This is explained by the structural formula (1) where only one hydrogen atom is attached to the oxygen atom and the remaining five to the carbon atoms. But in formula (2), the six hydrogen atoms occupy identical positions all being attached to the carbon atoms. It cannot be the formula of ethyl alcohol, for then we shall not be able to account for the fact that one and not all the hydrogen atoms are expelled by metallic sodium. As the structural formula (1) stands for ethyl alcohol, the structural formula (2) must stand for dimethyl ether, which is moreover found to be in accord with its properties.

Classification of organic compounds :

From the study of the structural formulae of various organic compounds, we find that they can be split up into distinct groupings of atoms which often preserve their identities in chemical reactions, passing out intact from one compound to another. These groupings of atoms are known as *compound radicals.* Some of these radicals, however, are found to be changed more readily than others in chemical reactions. They are said to be reactive or functional groups. The properties of an organic compound are mainly determined by the functional groups they contain. Hence organic compounds are classified according to their functional groups.

Family	Functional Group	Example
(1) Hydrocarbon	No functional group in particular. They are parents of other types of org. compds. which are formed by introducing different functional groups in place of H atoms.	CH_4(Methane) C_2H_6(Ethane) C_6H_6(Benzene)
(2) Alcohol	—OH(Hydroxyl)	CH_3OH Methyl alcohol C_2H_5OH Ethyl alcohol.
(3) Aldehyde	 $-C\lessgtr\begin{matrix}O\\H\end{matrix}$ (Aldehyde) (in short —CHO)	H.CHO Formaldehyde CH_3CHO Acetaldehyde
(4) Ketone	—CO—	$CH_3.CO.CH_3$ Acetone
(5) Acid	 $-C\lessgtr\begin{matrix}O\\OH\end{matrix}$ (carboxyl) (in short —COOH,	H.COOH Formic acid $CH_3.COOH$ Acetic acid
(6) Ester	—COOR	$CH_3COOC_2H_5$ Ethyl acetate
(7) Amine	$-NH_2$ (amino)	CH_3NH_2 Methyl amine $C_2H_5NH_2$ Ethylamine

In addition to functional groups, certain hydrocarbon radicals occur in most organic compounds. The formulae and names of some of them are given below.

Hydrocarbon radicals

Formula	Name
CH_3-	Methyl
C_2H_5-	Ethyl
C_3H_7-	Propyl
C_4H_9-	Butyl
C_6H_5-	Phenyl

The monovalent radicals derived from saturated aliphatic hydrocarbons are known as *alkyl radicals*. The first four (methyl to butyl) of the above radicals are alkyl radicals. They are represented usually by the symbol R.

Two broad divisions of organic compounds :

(1) *Aliphatic compounds*—they include all open chain compounds *e g.*, ethyl alcohol, $CH_3.CH_2OH$, acetic acid, $CH_3.COOH$ etc.

(2) *Aromatic compounds*—they are closed chain compounds containing one or more benzene rings, *e.g.*, benzene, naphthalene etc.

Saturated and unsaturated compounds :

Now in an organic compound, all the carbon atoms may be joined by single bonds or there may be one or more pairs of carbon atoms joined by double or triple bonds. The former class of compounds, for example, methane, CH_4, ethane, $CH_3.CH_3$ are saturated because they cannot react by addition, but only by substitution, *i e.*, by exchanging their hydrogen atoms for other atoms or groups. The latter class of compounds, for example, ethylene, $H_2C=CH_2$, acetylene, $HC\equiv CH$ are unsaturated, because they can react by addition, *i,e* , by combining with atoms of elements or groups without lossing anything.

Sources of Organic Compounds :

At one time, not long ago, the only source of organic compounds was nature, that is, the animate world of plants and animals ; for example, alcohol was obtained from sugar, glycerol from fats, cane sugar from sugar-canes etc. The number of pure organic compounds then known was comparatively small not more than a few dozens at the most. Since the historic synthesis of urea by Wohler in 1828, increasing number of organic compounds are being prepared synthetically. Synthetic organic compounds to-day far outnumber the natural products. Many organic compounds (for example, indigo) obtained originally from natural sources are now being prepared synthetically at a much lesser cost.

For some organic compounds, however, such as those which constitute our chief food-stuffs—carbohydrates, proteins, fats—we have to depend still on nature.

The chief natural sources of organic compounds are :

(1) **Petroleum** :—Huge quantities of petroleum are recovered from the bosom of the earth each year. By and large, petroleum is a mixture of saturated open chain hydrocarbons (paraffins). These hydrocarbons are comparatively unreactive. They are broken down into smaller units of reactive unsaturated hydrocarbons (olefins) by a process of thermal decomposition known as *cracking*. The latter hydrocarbons form the basic materials for the preparation of chemicals (*petrochemicals*) now used extensively for the manufacture of plastics, synthetic rubber, dyes, drugs etc.

(2) **Coal**.—The destructive distillation of coal furnishes as a by-product coal tar (see manufacture of coal gas, page, 222).

Coal tar contains many valuable aromatic organic compounds such as benzene, toluene, naphthalene, anthracene, phenol etc. These substances have been turned into valuable dyes, drugs, plastics, rubber etc. (see coal tar distillation, later).

(3) **Wood**.—Various basic organic substances are recovered as by-products when wood is subjected to destructive distillation for the production of charcoal for which there is an unlimited demand all the world over.

Wood distillation :

Hard wood, air dried to 15 to 20% moisture are heated in steel retorts gradually to about 450°C. The process, being exothermic, external heating is only necessary at the start. The distillation is continued for about 24 hours.

The following products are obtained :—

(i) Inflammable gases such as methane, CO, H_2 etc., which are mainly used for heating the retorts.

(ii) A liquid distillate which separates into two layers :

(*a*) A reddish brown watery liquid at the top known as *pyroligneous acid*.

Pyroligneous acid is an aqueous mixture of methyl alcohol (2-4%), acetone (0·5%), acetic acid (10%) and many other less important substances. Once, pyroligneous acid constituted the exclusive source of the substances mentioned above, but due to the discovery of synthetic processes for the manufacture of these articles, it has lost its former importance. The distillation of wood is now mainly carried out to meet the universal demand for charcoal. The recovery of methyl alcohol, acetic acid etc, from pyroligneous acid has been discussed in appropriate places (see text later).

(*b*) Wood tar (contains creosote) which settles at the bottom and is used for preserving timber.

(*c*) Wood charcoal.

Demonstration of wood distillation on a small scale :

The process of wood distillation may be demonstrated by the help of the following apparatus (fig. 118).

The upper flask (*a*) is half filled with saw dust and heated by means of a large Bunsen Burner. Gases begin to evolve within a short time and a tarry distillate collects in the receiver (*b*). The distillate in (*b*) separates into two layars on standing (an aqueous layer at the top and tar at the bottom). Uncondensed vapours are led through the water condenser when further condensation takes place.

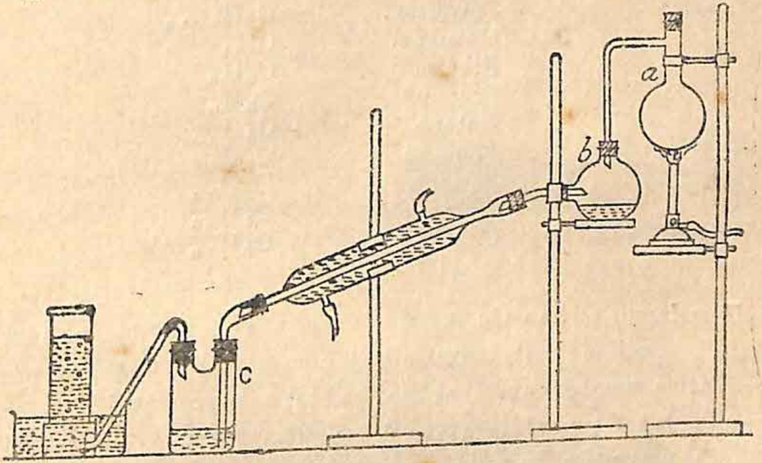


Fig. 118—Wood distillation on a small scale,

The residual gas after being freed from CO_2 by passage through alkali is collected over water.

Exercise

What is the functional group present in (*a*) an alcohol, (*b*) a ketone and (*c*) an ester ? Write the structural formula of a compound in each case.

Cal. Pre-U,, 1965

CHAPTER XXXVI

HYDROCARBONS

Hydrocarbons are compounds containing only carbon and hydrogen. They are of many kinds—(1) *open chain* or *aliphatic* and (2) *closed chain.*

Aliphatic hydrocarbons may be divided again as *saturated* and *unsaturated*, whereas the most important section of cyclic hydrocarbons are known as *aromatic hydrocarbons.*

Saturated aliphatic hydrocarbons are known as *paraffins.* The simplest paraffin is, methane, CH_4. There are many others. Some of the simplest members with their formulae are noted below.

Paraffins,	C_nH_{2n+2}
Methane	CH_4
Ethane	C_2H_6
Propane	C_3H_8
Butane	C_4H_{10}
Pentane	C_5H_{12}
Hexane	C_6H_{14}
Heptane	C_7H_{16}
Octane	C_8H_{18}
etc	etc.

Homologous series—On examination of the above table of paraffins, it will be noticed that there is a difference of CH_2 between any two consecutive members and that they can all be represented by a general formula of the type C_nH_{2n+2}. A set of compounds having similar chemical properties in which succeeding members differ by CH_2 is known as a *homologous series.* The organic compounds can all be grouped into several homologous series, each series containing sometimes hundreds of compounds. This fact has made the study of organic compounds comparatively easy because it has done away with the necessity of studying each and every compound separately. By studying one or two important compounds from each series, we can gather a fair knowledge of the rest. The students will notice some sort of a parallel phenomenon to the homologous series in the halogen family, but the halogen family consists of only four members—fluorine, chlorine, bromine and iodine.

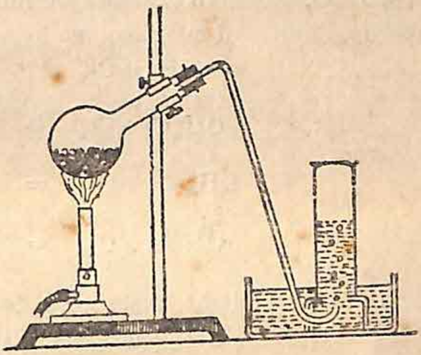
Saturated hydrocarbon

Methane or Marsh gas, CH_4 :

Methane is found to rise in bubbles from marshy lands where it is formed by the decay of dead organic matter under stagnant pool of water. It is a constituent of natural gas which issues from petroleum wells as well as from crevices of the earth's crust. It is present in coal mines where it forms with air explosive mixtures which have caused many serious colliery explosions. It is, therefore dreaded by the miners who call it '*fire damp*'.

Preparation—(1) It is usually prepared by heating a mixture of anhydrous Sodium acetate and Soda-lime.

Laboratory Method—Take an intimate mixture of 4 parts by wt. of Soda lime and 1 part by wt. of anhydrous (*fused*) Sodium acetate in a hard glass test tube, or a Copper flask, fitted with a delivery tube (fig. 119). Heat the mixture strongly. Methane is evolved, and, when all the air is expelled from the flask, collect the gas by the displacement of water.



Fig, 119—Preparation of methane

$$\underset{\text{(Sodium acetate)}}{CH_3COONa} + NaOH = CH_4 + Na_2CO_3.$$

N. B.—Although NaOH is written in the above equation, soda-lime is used in practice, for latter prevents the mixture from fusing.

Impurities present in Marsh gas.—The gas, thus obtained, is not pure. It contains Hydrogen, Ethylene, Acetylene, and moisture as impurities.

Removal of Impurities—The impurities can be removed by passing the gas through—(*i*) *Ammoniacal* cuprous chloride sol. (to absorb acetylene) ; (*ii*) *fuming* Sulphuric acid (to absorb Ethylene and moisture) ; and (*iii*) solid KOH. It is then collected over Mercury. It, however, still contains Hydrogen.

To remove this Hydrogen from Marsh gas, add excess of *pure* Oxygen and pass the mixture over Palladium black or Palladium asbestos at 100°C when Oxygen combines with the whole of Hydrogen but does not react with CH_4. Pass the resultant gases through alkaline pyrogallate sol. to absorb excess of Oxygen. Now dry CH_4 by conc. H_2SO_4 and collect it over Mercury.

(2) Very pure methane can be prepared by dropping a mixture of methyl iodide and methyl alcohol over Zn/Cu or Hg/Al couple.

$$CH_3I + 2H = CH_4 + HI$$

(3) By the action of water on aluminium carbide.

$$Al_4C_3 + 12H_2O = 4Al(OH)_3 + 3CH_4$$

Properties.—Methane is a colourless, odourless gas, half as light as air. It is practically insoluble in water. It burns with a non-luminous flame. With air or oxygen, it forms an explosive mixture.

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$

Methane is a saturated compound and as such quite inactive and is not attacked by most reagents under ordinary connitions. It can react only by giving up a hydrogen atom in place of an atom of another substance taken up. The process is called *substitution.*

For example, in presence of diffuse sunlight, chlorine replaces the hydrogen atoms of methane one by one.

$$CH_4 + Cl_2 = \underset{\text{(Methyl chloride)}}{CH_3Cl} + HCl$$

$$CH_3Cl + Cl_2 = \underset{\text{(Methylene chloride)}}{CH_2Cl_2} + HCl$$

$$CH_2Cl_2 + Cl_2 = \underset{\text{(Chloroform)}}{CHCl_3} + HCl$$

$$CHCl_3 + Cl_2 = \underset{\text{(Carbon Tetrachloride)}}{CCl_4} + HCl$$

In direct sunlight, explosion takes place—

$$CH_4 + 2Cl_2 = C + 4HCl.$$

In dark, however, no reaction occurs.

Uses.—In recent years, methyl alcohol and formaldehyde are being manufactured from methane.

Unsaturated hydrocarbon

Ethylene, $H_2C=CH_2$

Ethylene occurs in small quantities in coal gas.

Preparation : Laboratory Method.—Heat *carefully* a mixture of 1 part by vol. of Ethyl alcohol and about 3 parts by vol. of conc. H_2SO_4 in a flask, fitted with a dropping funnel and a delivery tube on a *sand bath* to about 170°C. Put in a few glass beads to prevent frothing up of the liquid. Conc. Sulphuric acid abstracts the elements of water from Ethyl alcohol, and Ethylene is liberated. To get *more* gas, drop a mixture of *equal vols.* of alcohol and conc. H_2SO_4 from a dropping funnel into the flask.

The gas, thus obtained, is not pure. It contains CO_2 and SO_2 as impurities. Pass the gas through Caustic soda solution to free it from the impurities and then collect it over water.

$$C_2H_5(OH) + H_2SO_4 = C_2H_4 + (H_2SO_4 + H_2O)$$

N. B.—Instead of H_2SO_4, *syrupy* H_3PO_4 or P_2O_5 may be used.

Properties—Ethylene is a colourless gas with a sweetish odour. It is almost as heavy as air. It is insoluble in water. It burns in air with a luminous flame, but it does not support combustion.

$$C_2H_4 + 3O_2 = 2CO_2 + 2H_2O$$

To satisfy the valencies of the two carbon atoms of ethylene, we must put a double bond between them. Compounds containing a double or a triple bond (*e.g.*, acetylene, see later) can react by addition and are unsaturated.

Being unsaturated, ethylene is very reactive in contrast to methane.

Chlorine adds to ethylene giving ethylene chloride which is an oily liquid.

$$C_2H_4 + C_2 = \underset{\text{Ethylene chloride,}}{Cl_2H_4Cl_2}$$

It is on account of this property, ethylene was named by its discoverers *olefiant* or oil producing gas. Hydrocarbons belonging to the ethylene family are known as **olefins.**

Bromine adds to ethylene in like manner giving ethylene bromide but iodine is without action on ethylene.

Ethylene is absorbed by fuming sulphuric acid, ethyl hydrogen sulphate, $C_2H_5.HSO_4$ being formed.

$$C_2H_4 + H_2SO_4 = C_2H_5.HSO_4$$

When ethylene is passed into cold alkaline potassium permanganate solution, it is oxidised to ethylene glycol, $C_2H_4\ (OH)_2$.

The colour of the pot. permanganate solution is discharged. This is a test for ethylene and other olefins. $C_2H_4 + H_2O + O \rightarrow C_2H_4(OH)_2$

Ethylene combines with ozone to form an ozonide.

$$C_2H_4 + O_3 = \underset{\text{Ethylene ozonide}}{C_2H_4O_3}$$

When a mixture of ethylene and hydrogen is passed over heated nickel (catalyst) at 200°C, ethylene adds two atoms of hydrogen and is converted thereby into the saturated hydrocarbon, ethane, C_2H_6

$$C_2H_4 + H_2 \xrightarrow{\text{Cat.}} C_2H_6$$

Uses.—Ethylene mixed with oxygen is used as an anaesthetic. It is also used for ripening green fruits and for the manufacture of ethyl alcohol, mustard gas and various solvents.

Acetylene, C_2H_2, $HC \equiv CH$

Acetylene does not occur in nature, but is purely an artificial product of the laboratory.

Preparation.—Acetylene is prepared on an industrial as well as on a laboratory scale by the action of water on calcium carbide, CaC_2. In the laboratory, small lumps of calcium carbide are taken inside a dry flask fitted with a cork, a dropping funnel and a delivery tube. Water is dropped gradually on the lumps of the calcium carbide from the funnel when acetylene is evolved. (fig. 120).

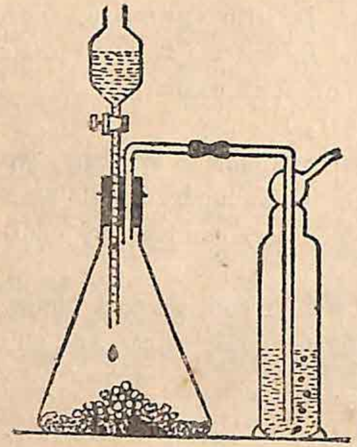


Fig. 120—Preparation of acetylene.

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$$

It is collected over water. As prepared above, it is impure.

Purification : Acetylene, as prepared by this method is impure and contains impurities such as small traces of ammonia, phosphine, H_2S etc.

It can be purified from those impurities by passing the gas (i) through copper sulphate solution and then (ii) through a tower containing bleaching powder and finally (iii) it is dried by P_2O_5. A thorough washing with water, however, makes it fit for use in industry.

Acetylene can be obtained on a small scale by striking an electric arc between two carbon electrodes in an atmosphere of hydrogen. (fig. 121). $2C + H_2 = C_2H_2 - 56{,}000$ cals.

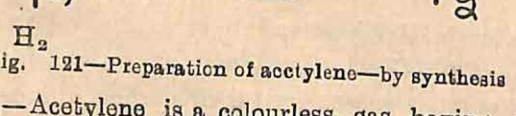


Fig. 121—Preparation of acetylene—by synthesis

Properties.—Acetylene is a colourless gas having a garlic odour when impure. Pure gas is said to have a sweet odour. It is insoluble in water but soluble in acetone. It can be easily liquefied by presure and cold.

Acetylene is an endotheremic compound. It contains more heat than the elements from which it is formed. Therefore, a large quantity of heat is set free when the molecule of acetylene breaks up. Acetylene is, therefore unstable, liable to explode when subjected to shock or pressure.

When a mixture of acetylene and oxygen is burnt, the flame becomes so hot that it can cut metal by melting.

$$2C_2H_2 + 5O_2 = 4CO_2 + 2H_2O.$$

When acetylene is mixed with hydrogen and the mixture is passed over spongy platinum, we get ethylene.

$$CH \equiv CH + H_2 \rightarrow CH_2 = CH_2$$

Like ethylene, acetylene adds halogens. Four atoms of a halogen are added in two instalments.

$$C_2H_2 \xrightarrow{Br_2} \underset{\text{Acetylene dibromide}}{C_2H_2Br_2} \xrightarrow{Br_2} \underset{\text{Acetylene tetrabromide}}{C_2H_2Br_4}$$

With Cl_2, acetylene ordinarily reacts with explosive violence forming carbon and HCl. $C_2H_2 + Cl_2 = 2C + 2HCl$. In presence of Kieselguhr (a kind of porous earth) acetylene, however, adds chlorine giving in two steps acetylene tetrachloride, $CHCl_2.CHCl_2$, which is sold as a non-inflammable solvent under the name, **Westron.**

$$CH \equiv CH \xrightarrow{Cl_2} CHCl = CHCl. \xrightarrow{Cl_2} CHCl_2 .\ CHCl_2$$

Acetylene adds one molecule of hydroiodic acid to form vinyl iodide, $CH_2 = CHI$, which again adds another molecule of the same substance yielding finally ethylidene iodide, $CH_3 .\ CHI_2$

$$CH \equiv CH + HI \rightarrow CH_2 = CHI$$

$$CH_2 = CHI + HI \rightarrow CH_3 .\ CHI_2 .$$

In the second step, the iodine atom (negative part of the molecule added) attaches itself to the carbon atom containing smaller number of carbon atoms (*Markownikoff's rule*).

In the same way, conc. H_2SO_4 reacts with acetylene giving finally ethylidene sulphate, $CH_3 .\ CH\,(HSO_4)_2$.

$$CH \equiv CH \xrightarrow{H_2SO_4} CH_2 = CH.HSO_4 \xrightarrow{H_2SO_4} CH_3 - CH(HSO_4)_2$$

When acetylene is passed into an ammoniacal solution of cuprous chloride, a red ppt. of cuprous acetylide is obtained.

$$C_2H_2 + Cu_2Cl_2 = \downarrow \underset{\text{Red ppt}}{C_2Cu_2} + 2HCl$$

Ammoniacal $AgNO_3$ solution gives a white ppt. of silver acetylide, C_2Ag_2 in like manner.

$$C_2H_2 + 2AgNO_3 = \uparrow C_2Ag_2 + 2HNO_3$$

Acetylene adds a molecule of water to form acetaldehyde when it is passed into warm mercuric sulphate solution in dilute sulphuric acid.

$$C_2H_2 + H_2O = CH_3.CHO$$

When acetylene is passed through a red hot tube, three molecules of acetylene join up to form benzene, C_6H_6. $3C_2H_2=C_6H_6$.

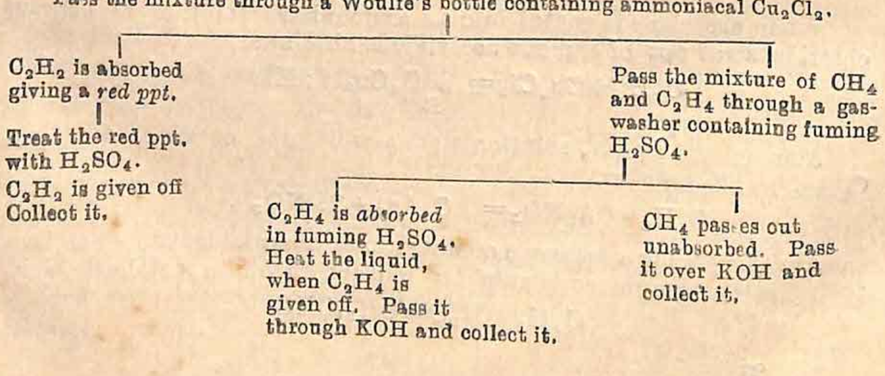
The process in which the molecules of the same substance combine to form a compound of higher mol. wt. is known as *polymerisation*.

Uses of acetylene—(i) It is used as an illuminant in carbide lamps, (2) for the production of oxy-acetylene flame for cutting and welding metals and (3) as a basic raw material for the preparation of acetaldehyde, acetic acid, acetone, industrial solvents and hosts of other organic chemicals.

Comparison between CH_4, C_2H_4 and C_2H_2

Methane	Ethylene	Acetylene
(1) Colourless, tasteless and odourless gas, *Sparingly soluble* in water.	(1) Colourless, tasteless gas having sweet odour. *Slightly* soluble in water.	(1) Colourless gas having a sweet smell, if pure. Impure gas has offensive smell. Dissolves in its *own vol.* of H_2O.
(2) Much lighter than air. (Density = 8).	(2) Nearly as heavy as air. (Density = 14)	(2) Lighter than air. (Density = 13)
(3) It is a *saturated* compound and gives *substitution products* with the halogens.	(3) It is an unsaturated compound and gives *additive compounds* with the halogens.	(3) It is an unsaturated compound and gives *additive compounds* with the halogens.
(4) Burns in air with a non-luminous flame	(4) Burns in air with a luminous flame.	(4) Burns in air with a highly luminous and smoky flame.
(5) Explodes violently when mixed with *twice* its vol. of O_2 and fired.	(5) Explodes violently when mixed with *thrice* its vol. of O_2 and fired.	(5) Explodes violently when mixed with two-and-half times its vol. of O_2 and fired.
(6) Reacts with Cl_2 in *diffused* sunlight giving *substitution* products.	(6) Combines readily with Cl_2 giving an *additive* compounds,	(6) Gives an additive compounds with Cl_2 in solution in S_2Cl_2.

Separation of CH_4, C_2H_4 and C_2H_2 in a mixture



Pass the mixture through a Woulfe's bottle containing ammoniacal Cu_2Cl_2.

C_2H_2 is absorbed giving a *red ppt.*

Treat the red ppt. with H_2SO_4.

C_2H_2 is given off Collect it.

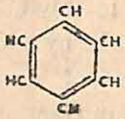
Pass the mixture of CH_4 and C_2H_4 through a gas-washer containing fuming H_2SO_4.

C_2H_4 is *absorbed* in fuming H_2SO_4. Heat the liquid, when C_2H_4 is given off. Pass it through KOH and collect it.

CH_4 passes out unabsorbed. Pass it over KOH and collect it.

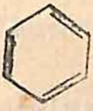
Aromatic Hydrocarbons.

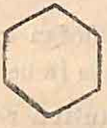
Benzene, C_6H_6



Benzene is a cyclic hydrocarbon. Its six carbon atoms are so joined as to form a regular hexagon. Each carbon atom in the ring is joined to two other carbon atoms. To one it is joined by a single bond, to the other by a double bond. Each carbon atom carries a hydrogen atom. This formula of benzene shown above is due to Kekule'.

Kekule's formula for benzene has some defects, but it is the best of of all formulae proposed so far. The defects of Kekule's formula can be explained by the modern concept of resonance ; but it is much beyond the scape of this book. Often for the sake of simplicity and also to spare time, benzene is represented by a simple hexagon. Double bonds may or may not be shown as depicted below.





At each of the six corners of the hexagon, we are to suppose that there is one carbon atom attached to a hydrogen atom.

Occurrence.—Benzene occurs in coal tar from which it is recovered by fractional distillation (see coal tar distillation, later).

Preparation.—Benzene can be prepared in the laboratory on a small scale by the following reactions.

(1) By passing acetylene through a red hot tube

$$\underset{\text{Acetylene}}{3C_2H_2} \rightarrow \underset{\text{Benzene}}{C_6H_6}$$

(2) By distilling benzoic acid with soda lime

$$\underset{\text{Benzoic acid}}{C_6H_5.COOH} + CaO \rightarrow \underset{\text{Benzene}}{C_6H_6} + CaCO_3$$

(3) By distilling phenol with zinc dust

$$\underset{\text{Phenol}}{C_6H_5OH} + Zn \rightarrow \underset{\text{Benzene}}{C_6H_6} + ZnO$$

Properties.—Benzene is a colourless oily liquid having a characteristic odour. It is insoluble in water, but soluble in ether, alcohol and other organic solvents. It boils at 80·4°C

Reactions.—Benzene is an unsaturated hydrocarbon and like ethylene ought to give mainly additive reactions, but it reacts by substitution more readily than by addition. It departs in many ways from the normal behaviours of an unsaturated hydrocarbon. Benzene gives only a few addition reactions in comparison with its substitution reactions.

Addition reactions.—(1) Chlorine and bromine in the presence of strong sunlight combine additively with benzene forming benzene hexachloride and hexabromide respectively. $C_6H_6 + 3Cl_2 = C_6H_6Cl_6$

(2) When a mixture of benzene vapour and hydrogen is passed over freshly reduced nickel heated to 200°, benzene takes up two, four and six hydrogen atoms giving finally cyclohexane.

$$C_6H_6 \xrightarrow[Ni]{H_2} C_6H_8 \xrightarrow[Ni]{H_2} C_6H_{10} \xrightarrow[Ni]{H_2} \underset{\text{Cyclohexane}}{C_6H_{12}}$$

(3) Benzene combines with three molecules of ozone to form a triozonide. $C_6H_6 + 3O_3 = \underset{\text{Benzene tri-ozonide}}{C_6H_6O_9}$

The addition reactions of benzene reveal the presence of three double bonds in benzene.

Substitution reactions.—(1) In presence of a catalyst, such as I_2, iron filings, or $AlCl_3$ (*halogen carriers*) chlorine or bromine substitutes the hydrogen atoms of benzene.

$$C_6H_6 + Cl_2 \rightarrow \underset{\text{Chlorobenzene}}{C_6H_5Cl} + HCl$$

$$C_6H_6 + Br_2 \rightarrow \underset{\text{Bromobenzene}}{C_6H_5Br} + HBr$$

Iodine, ordinarily, is without action on benzene.

(2) Benzene is readily attacked by hot and concentrated sulphuric acid producing benzene sulphonic acid.

$$C_6H_6 + \underset{\text{Sulphuric acid}}{HOSO_3H} = \underset{\text{Benzene sulphonic acid}}{C_6H_5SO_3H} + H_2O$$

In this reaction, the hydrogen atom of benzene has been substituted by—SO_3H (*sulphonic*) group.

One or more sulphonic groups may be introduced depending on the temperature of the reaction. The process is known as *sulphonation*.

(3) Concentrated nitric acid (in presence of concentrated sulphuric acid) reacts with benzene substituting the hydrogen atoms of the latter by—NO_2 (*nitro*) groups. The process is called *nitration*.

$$C_6H_6 + \underset{\text{Cold nitric acid}}{HONO_2} \xrightarrow{H_2SO_4} \underset{\text{Nitrobenzene.}}{C_6H_5NO_2} + H_2O$$

Up to three nitro groups may be introduced by varying the experimental conditions.

(4) In presence of anydrous aluminium chloride, benzene reacts with an alkyl halide to produce a higher homologue of benzene.

$$C_6H_6 + ClCH_3 \xrightarrow{AlCl_3} \underset{\text{Toluene}}{C_6H_5CH_3} + HCl$$

$$C_6H_5CH_3 + ClCH_3 \xrightarrow{AlCl_3} \underset{\text{Xylene}}{C_6H_4(CH_3)_2} + HCl$$

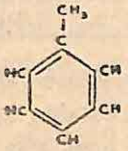
Benzene reacts with acetyl chloride in the presence of anhydrous aluminium chloride to produce *acetophenone* (a ketone).

$$C_6H_6 + ClCOCH_3 \xrightarrow{AlCl_3} \underset{\text{Acetophenone}}{C_6H_5COCH_3} + HCl$$

These reactions described under (4) are known as **Friedel-Crafts reaction.**

Uses of benzene—Benzene is used as a solvent of fat and also for dry washing woollen clothes. It is also used for the manufacture of nitrobenzene and through it aniline and other compounds required for the manufacture of dyes, drugs etc. It is mixed with petrol for use as motor spirit.

Toluene, C_7H_8,

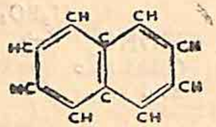


Toluene is a colourless liquid (b. p. 110°C) which occurs in and is obtained commercially from coal tar along with benzene. It is insoluble in water.

It can be obtained from benzene by Friedel-Crafts reaction (see above). It is very similar to benzene in properties.

Toluene is used for making the high explosive, T. N. T. It is also the starting material for the preparation of saccharin, several drugs and dyestuffs.

Naphthalene, $C_{10}H_8$,



Naphthalene is a white crystalline substance having a characteristic odour. It is insoluble in water. It is a well-known insecticide. It is the starting material for the preparation of artificial indigo and other dyes. In properties, it has many similarities with benzene.

Coal tar

Coal tar is obtained as a by-product in the manufacture of coal gas. It is also a by-product of coke ovens.

Coal tar is a vast store house of aromatic compounds, particularly of hydrocarbons such as benzene, toluene, naphthalene etc. It also contains in small quantities, basic substances such as pyridine and quinoline and acidic substances like phenol and cresols.

In order to recover the valuable components of coal tar, it is subjected to fractional distillation and the following fractions distilling between different temperature ranges are collected.

Temp range	Fraction	Chief components
110°—170°C	Light oil	Benzene, toluene
170°—230°C	Middle oil	Naphthalene, phenol
230°—270°C	Creosote oil	Cresols
above 270°C	Anthracene oil	Anthracene
Residue	Pitch	

Recovery of benzene and toluene from light oil fraction.—The light oil fraction contains benzene, toluene etc., together with alkaline and acidic impurities. The impurities are removed by washing with conc. H_2SO_4 followed by NaOH solution. It is finally washed with water till free from alkali. Now the purified light oil is fractionally distilled and benzene (b. p. 80·4°C) and toluene (b. p. 110°C) are separately collected.

Exercise.

1. Why is methane called marsh gas? Describe its preparation in the laboratory. What is the action of chlorine on methane?

2. How is acetylene prepared in the laboratory? How can it be synthesized from its elements? State its important properties, tests and uses.

3. Describe the changes which take place with equations when acetylene gas is passed into (*a*) mercuric sulphate solution in dilute sulphuric acid, (*b*) bromine water, (*c*) ammoniacal cuprous chloride and (*d*) ammoniacal silver nitrate solution.

4. Compare the properties of methane, ethylene and acetylene. How would you remove traces of acetylene from methane ?

5. What are hydrocarbons ? How do you classify them ? Why do you call ethylene and acetylene unsaturated compounds ?

6. How is benzene recovered from coal tar ? How can you prepare it in the laboratory ? Describe its important properties and uses.

7. Describe the preparation of acetylene. How may acetylene be converted into (*a*) ethane ; (*b*) acetaldehyde ; (*c*) benzene ; (*a*) ethylene ? *Cal. Pre-U. 1962*

8. What do you understand by a saturated and an unsaturated hydrocarbon ?

Describe the preparation of any unsaturated hydrocarbon you have studied and state its characteristic reactions with equations. *Cal, Pre-U , 1964*

9. How is acetylene prepared in the laboratory ? Give a neat sketch of the apparatus used. Explain with equations what happens when it is passed into :

(*a*) concentrated sulphuric acid : (*b*) ammoniacal solution of cuprous chloride. *Cal Pre-U 1966*

10. What is benzene ? Give its structural formula. How is it isolated from the light oil fraction of the coal tar ?

Describe with equations its reaction with (*a*) chlorine (*b*) concentrated sulphuric acid. *Cal. Pre-U., 1967*

11. Describe preparation and properties of ethylene. Mentiion at least three of its Chemical reactions. How does it differ from the hydrocarbon methane ? *Cal. Pre-U. 1970*

CHAPTER XXXVII

HALOGEN DERIVATIVES OF PARAFFINS

The halogen derivatives of paraffins are derived from the paraffins by replacing one or more hydrogen atoms by halogen atoms. We shall not here consider the fluorine derivatives, as they are less common and form a class by themselves.

Monohalogen derivatives of paraffins.—When only one hydrogen atom of a paraffin is substituted by a halogen atom we get a monohalogen derivative of a paraffin.

Monohalogen derivatives of paraffins have got the general formula, $C_nH_{2n+1}X$ where X = Cl, Br or I. They are usually known as *alkyl halides*. The names and formulae of some simple alkyl halides are given in the table below :

Methyl chloride	CH_3Cl	Methyl bromide	CH_3Br	Methyl iodide	CH_3I
Ethyl ,,	C_2H_5Cl	Ethyl ,,	C_2H_5Br	Ethyl ,,	C_2H_5I
Propyl ,,	C_3H_7Cl	Propyl ,,	C_3H_7Br	Propyl ,,	C_3H_7I

Preparation.—Alkyl halides can be prepared by the direct action of a halogen on paraffins in presence of diffused sunlight. It is however, difficult to stop the reaction at the desired stage. Consequently, higher halogen derivatives are produced at the same time. Alkyl halides are generally prepared more conveniently by the action of a halogen hydracid or a phosphorus halide on an alcohol.

(1) $C_2H_5OH + HCl = C_2H_5Cl + H_2O$

(2) $C_2H_5OH + PCl_5 = C_2H_5Cl + POCl_3 + HCl$

It is necessary to remove the element of water produced by suitable dehydrating agents like zinc chloride or sulphuric acid.

Physical properties.—The lower members of alkyl halides are generally liquid at the ordinary temperature with the exception of methyl chloride, methyl bromide and ethyl chloride which are gaseous at this temperature. Higher members are solid. The lower members have got a sweet ethereal odour. They are almost insoluble in water. Alkyl chlorides are slightly lighter than water, others are denser than water.

Reactions.—Unlike the paraffins, alkyl halides are highly reactive. They undergo a number of reactions several of which are of the double decomposition type (metathesis) in which the halogen atom is replaced by other groups, such as —OH,—CN,—NH_2 etc. Hence they are useful synthetic reagents. The reactions however, do not take place easily. The reactants in some cases have to be heated in a sealed tube. Some of the important reactions of alkyl halides are noted below, taking ethyl bromide as an example.

$$C_2H_5Br + NaOH\ (\text{aqueous}) = \underset{\text{Ethyl alcohol}}{C_2H_5OH} + NaBr$$

$$C_2H_5Br + KCN\ (\text{alcoholic}) = \underset{\text{Ethyl cyanide}}{C_2H_5CN} + KBr$$

$$C_2H_5Br + NH_3\ (\text{alcoholic}) = \underset{\text{Ethyl amine}}{C_2H_5NH_2} + HBr$$

Dihalogen derivatives of Paraffins—Methane forms only one type of dihalogen derivatives *e.g.*, methylene chloride, CH_2Cl_2, methylene bromide, CH_2Br_2 and methylene iodide, CH_2I_2. These compounds have no isomers. But ethane can give rise to two types of dihalogen derivatives according as the two halogen atoms are attached (i) both to the same carbon atom or (ii) separately one to each carbon atom.

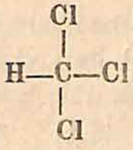
(i) CH_3CHX_2(ethylidene halide).

(ii) CH_2XCH_2X(ethylene halide).

The dihalogen derivatives are not important. We pass on to trihalogen derivatives.

Trihalogen Derivatives of Paraffins.—The trihalogen derivatives of methane are very important, particularly, the chloro-and the iodo-derivative. They are known as chloroform, $CHCl_3$ and iodoform, CHI_3 respectively. The tribromo-derivative, bromoform $CHBr_3$ is similar to chloroform and iodoform but it has very little use.

Chloroform, $CHCl_3$,



$$\begin{array}{c} Cl \\ | \\ H—C—Cl \\ | \\ Cl \end{array}$$

Chloroform is the trichloro-derivative of methane.

Preparation.—Pure chloroform required for anaesthetic purpose is obtained by distilling chloral $CCl_3.CHO$ with caustic soda solution.

$$\underset{}{CCl_3.CHO + NaOH = CHCl_3 + \underset{\text{Sod. formate}}{HCOONa}}$$

In the laboratory, chloroform is obtained by distilling ethyl alcohol (or acetone) with a paste of bleaching powder with water.

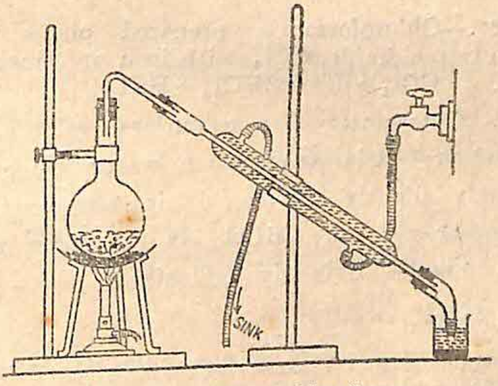


Fig. 122—Prepartion of chloroform

The bleaching powder supplies both chlorine and lime.

Chloral is supposed to be produced at first which is finally decomposed by lime.

$$CH_3.CH_2OH + Cl_2 = \underset{\text{Acetaldehyde.}}{CH_3.CHO} + 2HCl$$

$$CH_3CHO + 3Cl_2 = \underset{\text{Chloral}}{CCl_3\,CHO} + 3HCl$$

$$2CCl_3.CHO + Ca(OH)_2 = 2CHCl_3 + \underset{\text{Cal. formate.}}{(HCOO)_2Ca}$$

When acetone is used, the following series of reactions are supposed to take place.

$$CH_3.CO.CH_3 + 3Cl_2 = \underset{\text{Trichloroacetone.}}{CCl_3CO.CH_3} + 3HCl$$

$$2CCl_3.CO.CH_3 + Ca(OH)_2 = 2CHCl_3 + \underset{\text{Cal. acetate.}}{(CH_3.COO)_2Ca}$$

Experiment.—A strong sample of bleaching powder (300 gms.) is made into a paste with water (1 litre) and placed in a round-bottomed flask fitted with a delivery tube leading to a condenser (Fig. 122).

Ethyl alcohol (60 c.c) or acetone (65 c. c.) is then gradually added and the flask is cautiously heated on a sand bath till the reaction starts with great vigour. The flask is cooled if frothing is excessive. When the reaction has subsided, the mixture is heated gently when chloroform mixed with water, unchanged alcohol (or acetone) etc, distils over and collects under water in the receiver. The distillation is continued till no more oily drops pass over.

The lower layer of chloroform is then separated with the aid of a separating funnel, washed several times with dilute caustic soda solution and then with water. It is finally dried over fused calcium chloride and redistilled.

Manufacture.—Chloroform is prepared on a lage scale by reducing carbon tetrachloride, CCl_4 with iron in presence of a little acid and water. $CCl_4 + 2H = CHCl_3 + HCl$.

Properties.—Chloroform is a colourless, volatile liquid having a sweet sickly odour. It is heavier than water (Sp. gr.=1·5 at 15°), in which it is only slightly soluble. It is, however, readily soluble in alcohol and ether. It boils a 61°C. It is almost non-inflammable. Its vapour can be ignited only with difficulty.

(1) *Action of Air.*

In presence of sunlight and air, chlorofrom decomposes into carbonyl chloride and hydrochloric acid.

$$2CHCl_3 + O_2 = 2COCl_2 + 2HCl$$

Both the products are poisonous. Chloroform required for anaesthetic purpose should therefore, be stored in a cool dark place, in amber-coloured bottles full to the stopper with no air inside.

Pure chloroform does not give any ppt. with $AgNO_3$ solution.

When boiled with aniline and alcoholic potash, intolerable smell of phenyl isocyanide (carbylamine), C_6H_5NC is given out.

$$CHCl_3 + C_6H_5NH_2 + 3KOH \rightarrow \underset{\text{Phenyl isocyanide}}{C_6H_5NC} + 3KCl + 3H_2O$$

(2) *Action of Alkali*

Chloroform is decomposed by the action of concentrated and hot caustic potash solution into potassium formate, potassium chloride and water.

$$CHCl_3 + 4KOH \rightarrow 3KCl + 2H_2O + \underset{\text{Pot. formate}}{HCOOK}$$

(3) *Action of reducing agents.*

When reduced by a strong reducing agent, for example, by zinc dust and water, chloroform is reduced to methane.

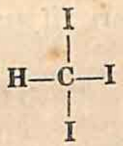
$$CHCl_3 + 6H \rightarrow CH_4 + 3HCl.$$

Tests.—*Carbylamine test*—When chloroform is warmed with aniline and alcoholic potash or soda, intensely foul odour or phenyl isocyanide or phenyl carbylamine is perceived.

$$C_6H_5N \vdots H_2 \vdots + C \vdots HCl_3 + 3KOH \rightarrow \underset{\text{Phenyl isocyanide}}{C_6H_5NC} + 3KCl + 3H_2O$$

Uses.—Chloroform is used as an anaesthetic in surgery. It is also used as a solvent, particularly, for oils and resins.

Iodoform, CHI$_3$,



$$H-\overset{\displaystyle I}{\underset{\displaystyle I}{C}}-I$$

Preparation.—It is prepared by the action of iodine and alkali on ethyl alcohol or acetone.

$$CH_3CH_2OH \xrightarrow{I_2} CH_3.CHO \xrightarrow{I_2} CI_3\,CHO \xrightarrow{NaOH} CHI_3$$

Iodoform is a golden yellow crystalline substance with a characteristic odour. It is insoluble in water.

It is used as an antiseptic in surgery.

Exercise.

1. How is pure chloroform prepared ? What happens when it is left in contact with air ? How is chloroform stored ? State its uses and tests.

2. What is iodoform ? How is it prepared ? State its uses.

3. Describe the preparation of chloroform from ethyl alcohol. How does chloroform react with (*a*) alcoholic caustic potash and (*b*) aniline ? Give equations.

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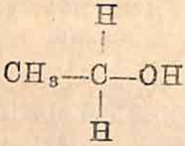
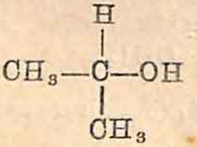
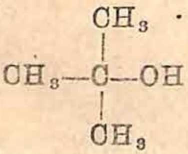
CHAPTER XXXVIII

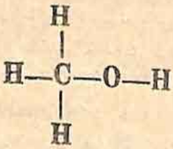
ALCOHOL

An alcohol is a hydroxy derivative of a hydrocarbon. An alcohol is classified as mono-, di-, trihydric etc., according to the number of $-OH$ groups present.

Formula	Name	Class
CH_3OH C_2H_5OH	Methyl alcohol Ethyl alcohol	Monohydric
$\begin{array}{l}CH_2OH\\ \vert\\ CH_2OH\end{array}$	Ethylene glycol	Dihydric
$\begin{array}{l}CH_2OH\\ \vert\\ CHOH\\ \vert\\ CH_2OH\end{array}$	Glycerol	Trihydric

Alcohols are also classified according to the number of hydrogen atoms attached to the carbon atom carrying the hydroxyl group; if the number is *two* (three in methyl alcohol), the alcohol is primary, if *one*, it is secondary; if *none*, then it is tertiary.

Formula	Name	Class
 $\begin{array}{c}H\\ \vert\\ CH_3-C-OH\\ \vert\\ H\end{array}$	Ethyl alcohol	Primary
 $\begin{array}{c}H\\ \vert\\ CH_3-C-OH\\ \vert\\ CH_3\end{array}$	Isopropyl alcohol	Secondary
 $\begin{array}{c}CH_3\\ \vert\\ CH_3-C-OH\\ \vert\\ CH_3\end{array}$	Tertiary butyl alcohol	Tertiary

Methyl alcohol, CH_3OH, 

$$\begin{array}{c}H\\ \vert\\ H-C-O-H\\ \vert\\ H\end{array}$$

Preparation: (*a*) *From pyroligneous acid.* This was once the only source of methyl alcohol. It has lost its former importance due to the discovery of a synthetic process of manufacture of methyl alcohol from water gas (see below).

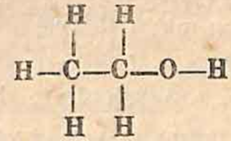
Pyroligneous acid contains 2—4% of methyl alcohol along with water, acetic acid and acetone. First of all the acetic acid is converted into non-volatile calcium acetate by lime and methyl alcohol and acetone are distilled off. Subsequently methyl alcohol is freed from most of acetone and water by repeated fractional distillation over quicklime. Methyl alcohol thus obtained, however, is liable to contain a little acetone.

(*b*) *By synthesis from water gas.*

Water gas is mixed up with half its volume of hydrogen gas and the mixture is passed over a catalyst consisting of a mixture of zinc oxide and chromium oxide under high pressure (200 atmos) and at moderate temperature (450°C).

$$\underset{\text{Water gas}}{(CO+H_2)}+H_2 \rightarrow CH_2OH$$

Properties.—Methyl alcohol is a colourless, volatile, poisonous liquid (b. p. 65°C) having a wine-like odour. It is soluble in water in all proportions. In chemical properties, it resembles ethyl alcohol (see below).

Ethyl alcohol, C_2H_5OH, 

$$H-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-O-H$$

Ethyl alcohol is by far the most important alcohol. When we say only alcohol, we mean ethyl alcohol. It is the intoxicating principle of all wines. Hence, it is also called *spirit of wine*.

Preparation : From the oldest time, ethyl alcohol is prepared by a process known as fermentation in which the sugar such as glucose present in fruit juices is converted into ethyl alcohol and CO_2 gas through the agency of a complex organic catalyst known as *zymase*. This zymase is a very complex nitrogenous substance which is produced by a low grade minute organism, *yeasts*, when they are put

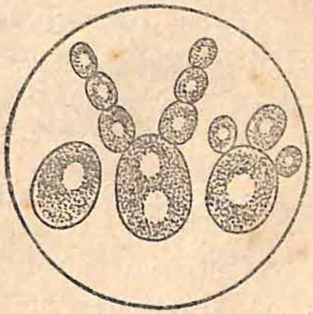


Fig. 123—Yeast cells

in a sugar solution. Yeasts as well as other organisms (plants and animals) usually produce numerous other organic catalyst of the type of zymase. These organic catalysts are known collectively as *enzymes*. In the process of fermentation, the liquid undergoing fermentation appears as if it is boiling though there is not much rise of temperature. On account of this phenomenon, the process is known as *fermentation* (Greek, *fervere=to boil*).

For the production of ethyl alcohol (wine), therefore, yeast is added to a dilute sugar (glucose) solution. The temp. is kept slightly above the ordinary (26°C). Alcoholic fermentation sets in within a short time through the activity of the enzyme, *Zymase* produced by yeast with steady evolution of CO_2 gas. At the end of fermentation, we get a dilute solution of alcohol.

$$C_6H_{12}O_6 = 2C_2H_5OH + 2CO_2$$

The dilute alcohol produced is then concentrated by fractional distillation (see below).

Starch-bearing grains or potatoes may also be used for producing alcohol, if another enzyme, '*diastase*' is also present. Diastase is present in germinating barley (malt).

(1) **From Starch.**—Industrial alcohol is manufactured from starch-bearing materials *e.g.*, cereals like rice, barley, wheat, maize and potatoes.

Starch, a carbohydrate having the formula $(C_6H_{10}O_5)n$ does not undergo fermentation by yeast directly. It can, however, undergo fermentation by yeast, if it is first converted into some form of sugar. For this purpose starch is made into a paste with water by boiling. It is then treated with **malt** (germinating barley) while hot (60°C) for about half an hour, when *diastase*, an enzyme present in malt converts starch mainly into malt sugar (maltose).

$$\underset{\text{Starch}}{2(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{\textit{Diastase}} \underset{\text{Maltose.}}{nC_{12}H_{22}O_{11}}$$

The diastase is now destroyed by boiling. The liquid is cooled to ordinary temperature and yeast is added. Fermentation sets in within a short time. The maltose is converted into alcohol in two stages. First it is converted into glucose by the enzyme *maltase* present in ordinary yeast and then the glucose is converted by the *zymase* of the yeast into alcohol and carbon dioxide gas.

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \rightarrow \underset{\text{Ethyl alcohol}}{2C_2H_5OH} + 2CO_2.$$

Small quantities of glycerol, succinic acid and higher alcohols. (fusel oil) are also produced at the same time.

The weak spirit (wash) obtained is submitted to fractional distillation in stills of special designs such as **Coffey's still** whereby alcohol of strength 90 per cent and above is obtained.

The alcohol as it is obtained from Coffey's still containing about 95·6 per cent of alcohol by volume is known as **rectified spirit.**

The last few per cents of water (4·4%) from a constant boiling mixture with alcohol and can not be removed by fractional distillation.

The amount of water in rectified spirit can be raduced to less than half percent by distillation over fresh quicklime. Alcohol so obtained is ordinarily known as **absolute alcohol**. The remaining quantity of water can be removed by distillation over metallic calcium.

(2) **From ethylene.**—Ethyl alcohol is now-a-days manufactured from ethylene. Ethylene gas is absorbed in concentrated sulphuric acid under pressure when ethyl hydrogen sulphate is formed.

$$C_2H_4 + H_2SO_4 = C_2H_5\,HSO_4.$$

The mixture is then diluted with water and boild. Ethyl hydrogen sulphate undergoes hydrolysis forming ethyl alcohol.

$$C_2H_5\,HSO_4 + H_2O = C_2H_5OH + H_2SO_4.$$

Sulphuric acid regenerated in the final step is used again after concentration.

Denatured spirit.—Ethyl alcohol is subjected to heavy excise duty in most countries which makes it too costly for use in industry. In order to avoid this difficulty, ethyl alcohol is rendered unfit for drinking purpose by the addition of obnoxious and unpalatable substances. Methyl alcohol, pyridine, raw rubber juice (caoutchouc) etc., are used for this purpose. The alcohol so treated is then sold duty-free for use in industry under the name, *denatured spirit* (*alcohol*).

Properties.—Ethyl alcohol is a colourless volatile liquid having a pleasant wine like odour. It boils at 78·3°C. It is miscible with water in all proportions. A contraction in volume takes place when ethyl alcohol is mixed with water.

Reactions :

(1) Metallic potassium or sodium reacts with ethyl alcohol liberating hydrogen. $2C_2H_5OH + 2Na = 2C_2H_5ONa + H_2$

(2) Phosphorous pentachloride and trichloride react with ethyl alcohol producing ethyl chloride. Hydrochloric acid is set free with the former reagent.

$$C_2H_5OH + PCl_5 = C_2H_5Cl + HCl + POCl_3$$

$$3C_2H_5OH + PCl_3 = 3C_2H_5Cl + \underset{\text{Phosphorous acid.}}{P(OH)_3}$$

(3) Although neutral in reaction, ethyl alcohol combines with acids to form compounds (esters) similar to salts in names and formulae, but otherwise quite different.

$$C_2H_5OH + HCl = \underset{\text{Ethyl chloride}}{C_2H_5Cl} + H_2O$$

$$CH_3COOH + HOC_2H_5 = \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O$$

(4) On oxidation with chromic acid *i.e.*, potassium dichromate and sulphuric acid, ethyl alcohol is converted first into acetaldehyde which is further oxidised by the prolonged action of the reagent into acetic acid. $2CH_3.CH_2OH + O_2 = 2CH_3.CHO + 2H_2O.$

$$2CH_3.CHO + O_2 = 2CH_3\,COOH.$$

(5) Concentrated sulphuric acid reacts with ethyl alcohol giving rise to different products under different conditions.

(*a*) When ethyl alcohol and conc. sulphuric acid are heated together in molecular proportions at 100°C, ethyl hydrogen sulphate is produced. $C_2H_5OH + H_2SO_4 = C_2H_5HSO_4 + H_2O.$

(*b*) When excess of ethyl alcohol is heated with concentrated sulphuric acid at 130°—140°C, diethyl either is produced.

$$C_2H_5OH + H_2SO_4 = C_2H_5HSO_4 + H_2O.$$

$$C_2H_5HSO_4 + HOC_2H_5 = C_2H_5.O.C_2H_5 + H_2SO_4.$$

(*c*) Ethylene is produced when ethyl alcohol is heated with an excess of concentrated sulphuric acid at 170°C.

$$C_2H_5OH + H_2SO_4 = C_2H_4 + [H_2O,H_2SO_4]$$

(*d*) When chlorine is passed into ethyl alcohol, trichloroacetaldehyde or chloral is produced.

$$CH_3.CH_2OH + Cl_2 = \underset{\text{Acetaldehyde}}{CH_3\,CHO} + 2HCl.$$

$$CH_3.CHO + 3Cl_2 = \underset{\text{Chloral}}{CCl_3\,CHO} + 3HCl.$$

(6) When distilled with bleaching powder made into a paste with water, ethyl alcohol yields chloroform. (see preparation of chloroform).

(7) In the same way, iodoform is produced when ethyl alcohol is warmed with iodine and an alkali. (see iodoform).

Uses —Ethyl alcohol is used,

(1) as a beverage,

(2) as a fuel in spirit lamps,

(3) as a substitute for petrol,

(4) as a solvent for resin, gum and other substances,

(5) in the preparation of tinctures, varnishes and perfumes,

(6) as a raw material for the preparation of chloral, chloroform, iodoform and ethylene etc.

Tests.—(1) *Iodoform test.*—When a sample of ethyl alcohol is warmed with iodine and an alkali, golden yellow crystals of iodoform with a characteristic odour are obtained on cooling.

(2) When ethyl alcohol is heated with benzoic acid in presence of concentrated sulphuric acid, the characteristic fruity odour of ethyl benzoate is given out.

Phenol, C_6H_5OH

Phenol is hydroxy benzene and resembles an alcohol in structure. In properties it differs widely from alcohol. It is distinctly an acid dissolving in caustic alkalis to form phenates.

$$C_6H_5OH + NaOH = \underset{\text{Sodium phenate}}{C_6H_5ONa} + H_2O.$$

It is also known as carbolic acid. It is a colourless crystalline substance having a characteristic odour. It, however, turns pink on exposure to air and light. It is a corrosive poison. It is used as a disinfectant and for the manufacture of a variety of plastics (bakelite), organic chemicals (salicylic acid) and explosives (picric acid).

Exercise.

1. What are alcohols and how are they classified ?

2. How is methyl alcohol prepared from water gas ? State its important physical and chemical properties. Mention its uses.

3. Describe the preparation of ethyl alcohol from starch. Why is it called spirit of wine ? Describe a property in which it resembles water.

4. State the action of the following on ethyl alcohol :—

(*a*) metallic sodium, (*b*) hydrochloric acid, (*c*) oxidising agents and (*d*) bleaching powder.

5. How is ethyl alcohol prepared ? Describe its properties and uses. How do you prepare ethyl acetate from ethyl alcohol ? What happens when ethyl acetate is treated with sodium hydroxide solution ? Explain with equations.

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6. How is ethyl alcohol obtained from glucose ? Describe with equations what happens when a mixture of aqueous ethyl alcohol and bleaching powder is distilled.

How does phosphorus pentachloride react with ethyl alcohol ? What information regarding its structure is obtained from this reaction ? *Cal. Pre-U., 1966.*

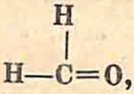
CHAPTER XXXIX

ALDEHYDES AND KETONES

If the two hydrogen atoms belonging to one of the end carbon atoms of a hydrocarbon are replaced by an oxygen atom, we get the formula of an aldehyde. If the hydrogen atoms, belong to a carbon atom which is not at the end, a ketone results.

$$\underset{\text{Propane}}{CH_3.CH_2.CH_3} \xrightarrow[+O]{-2H} \begin{cases} \underset{\text{Propionaldehyde}}{CH_3.CH_2.CHO} \\ \underset{\text{Dimethyl ketone}}{CH_3.CO.CH_3} \end{cases}$$

Aldehydes contain the functional group —CHO, and ketones $>C=O$. (keto) group.

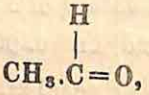


Formaldehyde, $H-\overset{\overset{\displaystyle H}{|}}{C}=O$, H.CHO

It is the simplest aldehyde. It is obtained by passing methyl alcohol vapour and air over heated platinum.

$$CH_3OH \xrightarrow{O} H.CHO + H_2O.$$

Formaldehyde is a gas soluble in water with an irritating smell. Its solution in water is used under the name *formalin* as an antiseptic for preserving biological and anatomical specimens. Formaldehyde is also used for the preparation of plastics. In chemical properties, it resembles acetaldehyde in most of its reactions.



Acetaldehyde, $CH_3.\overset{\overset{\displaystyle H}{|}}{C}=O$, $CH_3.CHO$

Acetaldehyde is a typical representative of the family.

Preparation.—(1) Acetaldehyde is prepared by oxidising ethyl alcohol with potassium dichromate and sulphuric acid.

$$3CH_3.CH_2OH + K_2Cr_2O_7 + 4H_2SO_4$$
$$= 3CH_3.CHO + K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O.$$

Experiment.—A distilling flask fitted with a tap funnel and a condenser joined to a receiver through an adaptor is set up as shown in fig. 124.

Coarsely powdered sodium dichromate (3 parts) and water (12 parts) are placed in the flask and a mixture of alcohol (3 parts) and concentrated sulphuric acid (4 parts) is added into it drop by drop from the tap funnel. The flask is heated gently on a sand bath to start the reaction. A vigorous reaction soon sets in. Ice cold water is now circulated through the condenser. A liquid containing acetaldehyde, alcohol and water collects in the receiver.

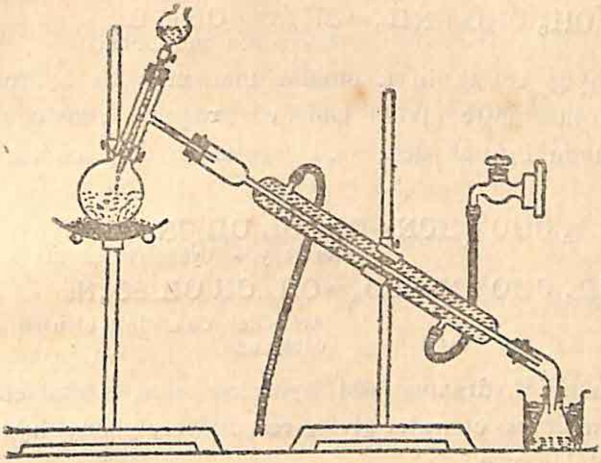


Fig. 124—Preparation of acetaldehyde.

The distillate is redistilled with a fractionating column on a water bath and the vapour which contains mainly acetaldehyde is passed into dry ether. The ethereal solution is saturated with ammonia gas when crystals of aldehyde-ammonia (*see below*) separate out. These crystals are washed with ether and then decomposed by distillation with dilute sulphuric acid. The distillate is then dried over anhydrous calcium chloride and redistilled.

(2) **From acetylene.**—Acetaldehyde is now prepared on a large scale by passing acetylene into warm (60°C) and dilute (20%) sulphuric acid in presence of mercuric sulphate as a catalyst. Acetylene combines with a molecule of water to produce acetaldehyde.

$$HC{\equiv}CH + H_2O \rightarrow CH_3.CHO.$$

(3) Acetaldehyde can also be prepared by the dry distillation of a mixture of calcium acetate and calcium formate.

$$\underset{\text{Cal. acetate}}{(CH_3.COO)_2Ca} + \underset{\text{Cal. formate}}{(HCOO)_2Ca} = \underset{\text{Acetaldehyde}}{2CH_3.CHO} + 2CaCO_3$$

Properties.—Acetaldehyde is a very volatile pungent smelling liquid, b. p., 21°C. It is soluble in water.

When reduced, it gives ethyl alcohol.

$$CH_3.CHO \xrightarrow{[\ 2H\ ]} CH_3.CH_2OH$$

It combines additively with ammonia giving a crystalline product—acetaldehyde-ammonia.

$$CH_3.CHO + NH_3 = \underset{\text{Acetaldehyde-ammonia}}{CH_3.CH(OH)NH_2}$$

Acetaldehyde reacts in a similar manner with hydrocyanic acid and sodium bisulphite giving additive products known respectively as acetaldehyde cyanohydrin and acetaldehyde sodium bisulphite compound.

$$CH_3.CHO + HCN = \underset{\text{Acetaldehyde cyanohydrin}}{CH_3.CH(OH)CN}$$

$$CH_3.CHO + NaHSO_3 = \underset{\substack{\text{Acetaldehyde sodium bisulphite}\\\text{compound}}}{CH_3.CH(OH)SO_3Na}$$

With phenyl hydrazine and hydroxylamine, acetaldehyde, however, reacts with loss of water giving respectively phenyl hydrazone and oxime of acetaldehyde.

$$CH_3.CHO + \underset{\text{Phenyl hydrazine}}{H_2N.NH.C_6H_5} \rightarrow \underset{\text{Acetaldehyde phenyl hydrazone}}{CH_3.CH = N.NH.C_6H_5} + H_2O$$

$$CH_3.CHO + \underset{\text{Hydroxylamine}}{H_2NOH} \rightarrow \underset{\text{Acetaldoxime.}}{CH_3.CH = NOH} + H_2O$$

Acetaldehyde is easily oxidised to acetic acid.

$$CH_3.CHO \xrightarrow{O} CH_3.COOH$$

Acetaldehyde is a reducing agent. It reduces alkaline copper hydroxide solution (*Fehling's soln.*) giving a red ppt. of cuprous oxide.

$$2CuO + CH_3.CHO = \downarrow \underset{\text{Red ppt.}}{Cu_2O} + CH_3.COOH$$

Fehling's solution is actually prepared by adding a mixture of strong caustic soda and *Rochelle salt* (sod. pot. tartrate) to copper sulphate solution.

Acetaldehyde also reduces ammoniacal silver nitrate solution depositing a bright mirror of silver.

$$Ag_2O + CH_3.CHO = 2Ag + CH_3COOH$$

N. B.—Ammoniacal $AgNO_3$ soln. is a solution of silver oxide in ammonium hydroxide.

Acetaldehyde undergoes polymerisation readily. Two products, one liquid, *paraldehyde*, $(CH_3.CHO)_3$ and another solid, *metaldehyde* $(CH_3.CHO)_4$ are obtained under different conditions.

Acetaldehyde restores the colour of Schiff's reagent, which is, really, a solution of magenta dye decolorised by SO_2.

Uses.—Acetaldehyde is used in the preparation of acetic acid, ethyl alcohol etc. Paraldehyde is used as a hypnotic and metaldehyde as a solid fuel.

Acetone: *dimethyl ketone, propanone*, $CH_3.CO.CH_3$, is the simplest ketone. It occurs, sometimes, in the urine of people suffering from acute diabetes. It is also a constituent of pyroligneous acid.

Preparation.—(1) In the laboratory and also industrially acetone is obtained by the dry distillation of calcium acetate.

$$\begin{array}{l} CH_3CO|O \\ CH_3|\overline{COO} \end{array}\!>Ca \rightarrow CH_3.CO.CH_3 + CaCO_3$$

Experiment.—About 100 gms. of dry calcium acetate are taken inside a retort joined to a Liebig's condenser and a receiver. The retort is slowly heated by a bunsen burner. Acetone distils over and collects in the receiver. (Fig. 125).

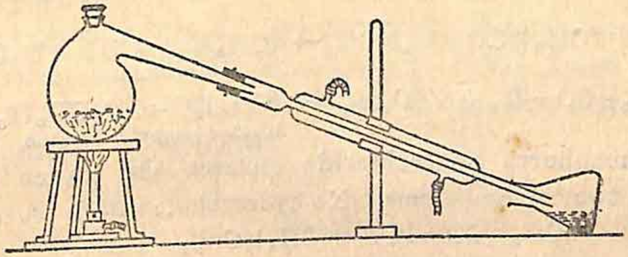


Fig. 125—Preparation of Acetone

The crude acetone is now purified by shaking it with a concentrated solution of sodium bisulphite. Sparingly soluble crystals of *sodium bisulphite* compound separate out.

$$(CH_3)_2CO + NaHSO_3 = \underset{\substack{\text{Sod. bisulphite compound} \\ \text{of acetone}}}{(CH_3)_2C(OH)SO_3Na}$$

The crystals are well pressed to remove adhering liquids and then distilled with sodium carbonate solution.

The distillate of pure aqueous acetone *thus obtained* is dried over fused calcium chloride and is then redistilled.

(2) Acetone is also made industrially along with butyl alcohol by a process of fermentation of maize (*Weizmann process*).

(3) It may be prepared also by the oxidation of isopropyl alcohol.

$$\underset{\text{Isopropyl alcohol}}{CH_3.CHOH.CH_3} \xrightarrow{[O]} CH_3.CO.CH_3 + H_2O.$$

Properties.—Acetone is a colourless, volatile liquid having a rather pleasant odour. It is miscible with water, alcohol and ether in all proportions. It boils at 56·5°C.

It is an excellent solvent for many organic substances, *e.g.* acetylene.

Reactions.—In the reactions noted below, acetone bears a close resemblance to acetaldehyde.

(1) **Addition reactions.**—Acetone combines *additively* with hydrocyanic acid and sodium bisulphite.

$$(CH_3)_2CO + HCN \rightarrow \underset{\text{Acetone cyanohydrin}}{(CH_3)_2C(OH)CN}$$

$$(CH_3)_2CO + NaHSO_3 \rightarrow \underset{\text{Acetone sod. bisulphite}}{(CH_3)_2C(OH)SO_3Na}$$

(2) **Reactions involving loss of water.**—Acetone forms an oxime with hydroxylamine and a phenyl hydrazone with phenyl hydrazine.

$$(CH_3)_2CO + H_2NOH \rightarrow \underset{\text{Acetoxime}}{(CH_3)_2C{=}NOH} + H_2O$$

$$(CH_3)_2CO + H_2N.NHC_6H_5 \rightarrow \underset{\text{Acetone phenylhydrazone}}{(CH_3)_2C{=}N.NHC_6H_5} + H_2O.$$

(3) **Phosphorus pentachloride** replaces the oxygen atom of acetone by two chlorine atoms. No hydrochloric acid is set free.

$$(CH_3)_2CO + PCl_5 \rightarrow (CH_3)_2C.Cl_2 + POCl_3$$

Reactions in which acetone differs from acetaldehyde :

(1) **Oxidation.**—When oxidised by a moderately strong oxidising agent, acetone in common with other ketones breaks down into a mixture of acids, each acid containing *a fewer* number of carbon atoms than the original ketone.

$$CH_3.CO.CH_3 + 2O_2 \rightarrow CH_3.COOH + CO_2 + H_2O.$$

(2) **Reducing action.**—Acetone does not reduce either ammoniacal silver nitrate solution or Fehling's solution.

(3) **Ammonia** does not form an *additive* compound with acetone, but reacts with loss of water to form complex compounds such as *diacetonamine*.

(4) **Condensation.**—Acetone unlike aldehydes does not undergo polymerisation, but gives a number of condensation products. Acetone in contact with NaOH or $Ba(OH)_2$ condenses to form *diacetonyl acetone.*

$$(CH_3)_2CO + CH_3.CO.CH_3 \rightarrow \underset{\text{Diacetonyl acetone}}{(CH_3)_2C(OH)CH_2.CO.CH_3}$$

Diacetonyl acetone when heated in presence of a little iodine loses water to form *mesityl oxide.*

$$(CH_3)_2C(OH)CH_2.CO.CH_3 \rightarrow \underset{\text{Mesityl oxide}}{(CH_3)_2C{=}CH.CO.CH_3} + H_2O$$

(5) **Reduction.**—On reduction, acetone gives a *secondary* alcohol, isopropyl alcohol, (acetaldehyde gives a *primary* alcohol).

$$CH_3.CO.CH_3 \xrightarrow{[2H]} \underset{\text{Isopropyl alcohol}}{CH_3.CHOH.CH_3}$$

Tests.—(1) A solution of I_2 in KI is added to a few c. c. of acetone and warmed. Now caustic soda solution or ammonia is added till the colour of I_2 is discharged. On cooling, yellow crystals of iodoform with characteristic odour separate. (Ethyl alcohol does not respond to this test if ammonia is used in place of caustic alkalis).

(2) *Legal's test.*—When a few drops of freshly prepared sodium nitroprusside solution is added to acetone (5 c.c.), and then the solution is made alkaline with caustic soda solution (1 c.c.), a ruby red colour is produced.

Uses.—Acetone is used in the preparation of chloroform, iodoform, ionone (synthetic perfume), sulphonal etc. ; in the storage of acetylene and as a solvent in the manufacture of smokeless powder (cordite), celluloid, paints and varnishes.

Exercise.

1. What is the functional group present in an aldehyde ? How is acetaldehyde prepared ? State the action of ammonia and phenyl hydrazine on acetaldehyde ?

2. What is Fehling's solution ? How is it prepared ? What happens when an aldehyde is warmed with Fehling's solution ? What is the action of Fehling's solution on acetone ?

3. What is a ketone ? Give the formula and name of the simplest ketone. How is it prepared in the laboratory ? How does a ketone differ from an aldehyde ?

4. Describe any method for the preparation of acetone ? How would you purify it ? Describe two reactions with equations by which you can distinguish between acetone and acetaldehyde. *Cal. Pre-U., 1961.*

5. What is the functional group present in an aldehyde ? How is acetaldehyde prepared ? Describe with equations its reaction with (*a*) ammonia, (*b*) hydrogen cyanide, (*c*) saturated solution of sodium bisulphite. *Cal. Pre-U., 1963.*

6. Describe how you would prepare acetaldehyde in the laboratory. Give a neat sketch of the apparatus. Discuss any two reactions of acetaldehyde. *Cal. Pre-U., 1965.*

7. State with equations the reactions when :—

(*a*) Calcium acetate is distilled dry ; (*b*) Acetone is treated with HCN, (*c*) Chloroform is heated with concentrated potassium hydroxide solution ; (*d*) Benzene is heated with concentrated sulphuric acid. *Cal. Pre-U., 1965.*

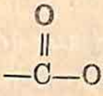
8. Give structural formulae of acetaldehyde and acetone. How is acetone prepared in the laboratory ? Describe with equations the reaction of acetone with (*a*) HCN ; (*b*) $NaHSO_3$. *Cal. Pre-U., 1967.*

CHAPTER XL

ORGANIC ACIDS

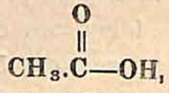
Most organic acids contain a carboxyl group as their functional group. Carboxyl group is made up of one *carbonyl* (—CO) group and one *hydroxyl* (—OH) group.

Its structure is



$-\overset{\overset{\displaystyle O}{\|}}{C}-OH$ though often it is written simply as $-COOH$.

More than one *carboxyl* group may be present in an organic acid. Acetic Acid contains one, oxalic acid two and citric acid as many as three carboxyl groups.



Acetic acid, $CH_3.\overset{\overset{\displaystyle O}{\|}}{C}-OH$, $CH_3.COOH$

Acetic acid is the longest known organic acid and is present in vinegar.

Vinegar : Vinegar is nothing but a dilute (6-7%) solution of acetic acid containing some flavouring matter.

Preparation : It is obtained by the oxidation of dilute alcohol (wine) through the agency of a complex organic catalyst produced by a class of micro-organism known as *Mycoderma Aceti*, the spores of which are present in air. At home, vinegar is produced by placing dilute alcoholic beverage like cidar or wine in an earthenware pot and adding mother of vinegar. The lid is loosely fitted to allow some access of air. The alcohol undergoes slow oxidation in presence of Mycoderma Aceti present in the mother of vinegar to yield dilute acetic acid, the whole process requiring months for completion.

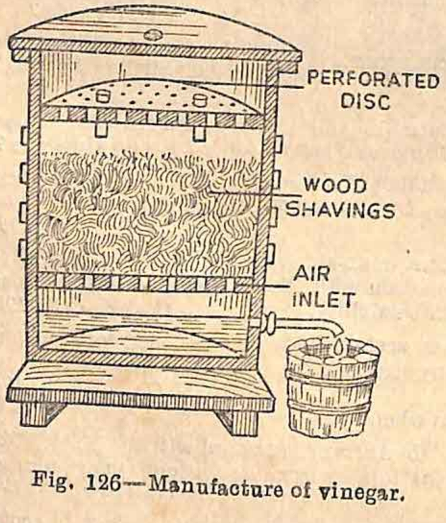


Fig. 126—Manufacture of vinegar.

In the Quick Vinegar Process, dilute alcohol is allowed to percolate through a hole in a wooden cask into beechwood shavings which have been previously soaked in vinegar. (Fig. 126). The beechwood shavings are interposed between two perforated shelves fitted midway to the inside wall of the cask. Air is forced upward through holes at the bottom of the cask. Rapid oxidation takes place. The liquid which emerges from the bottom is an aqueous solution of acetic acid commonly known as vinegar.

$$CH_3.CH_2.OH + O_2 \rightarrow CH_3.COOH + H_2O$$

Pure acetic acid, however, is never prepared from vinegar.

Preparation of Acetic Acid : (1) *From pyroligneous Acid. :—* At one time, acetic acid was obtained mainly from pyroligneous acid of wood distillation. Acetic acid in pyroligneous acid is neutralised by lime to form non-volatile cal. acetate, and methyl alcohol and acetone are distilled off. The crude cal. acetate is carefully ignited to burn off tarry matter. The grey acetate obtained, is distilled with mineral acid when dilute acetic acid is obtained. The dilute acid is neutralised with sodium carbonate and evaporated to crystallisation when hydrated sodium acetate crystals are obtained. The crystals are fused and distilled with conc. sulphuric acid when pure (glacial) acetic acid is obtained.

(2) *By Synthesis* : Now-a-days, the bulk of acetic acid is obtained from acetylene by way of acetaldehyde. Acetylene is passed into warm dilute (25%) sulphuric acid containing mercuric sulphate in solution. Acetyline takes up a molecule of water to yield acetaldehyde. Acetaldehyde is then heated to 60°C in presence of manganese acetate (catalyst) and air is blown in. Acetaldehyde is rapidly oxidised to acetic acid.

$$C_2H_2 + H_2O \xrightarrow[H_2SO_4]{HgSO_4} CH_3.CHO \xrightarrow[\text{Mn-salt}]{\text{Air}} CH_3.COOH$$

Properties.—Anhydrous acetic acid is a colourless liquid in our country though in cold countries in winter, it is a crystalline solid, melting at 16·5°C. It boils at 118°C. It has a characteristic vinegar-like odour. It is miscible with water, alcohol and ether in all proportions. A contraction in volume takes place when acetic acid is mixed with water so that the strength of an aqueous solution of acetic acid can not be found directly by a hydrometer. An aqueous solution containing 55 per cent acetic acid has the same density as the pure acid. (sp. gr. 1·08 at 0°C).

Acetic acid is corrosive and raises blisters on the skin. It is an excellent solvent and is used widely as such in organic preparations.

Reactions.—

(i) Acetic acid combines with alcohol in presence of concentrated sulphuric acid to form esters (alkyl acetates)

$$CH_3.COOH + HOC_2H_5 \overset{H_2SO_4}{\rightleftharpoons} \underset{\text{Ethyl acetate.}}{CH_3.COO.C_2H_5} + H_2O$$

(ii) Acetic acid reacts with phosphorus pentachloride to give acetyl chloride with liberation of hydrochloric acid.

$$CH_3.COOH + PCl_5 \rightarrow \underset{\text{Acetyl chloride.}}{CH_3.COCl} + POCl_3 + HCl$$

(iii) Acetic acid is a typical weak acid though it is strong enough to dissolve metals and metallic hydroxides.

$$2CH_3.COOH + Zn \rightarrow (CH_3.COO)_2Zn + H_2$$
$$CH_3.COOH + NaOH \rightarrow CH_3.COONa + H_2O$$

(iv) it decomposes metallic carbonates setting free CO_2 gas.

$$2CH_3.COOH + Na_2CO_3 \rightarrow 2CH_3.COONa + CO_2 + H_2O$$

(v) It presence of sunlight and catalysts, chlorine and bromine substitute the hydrogen atoms of the methyl group in acetic acid one by one yielding mono-, di-, and trichloro- and bromo-acetic acids respectively.

$$CH_3.COOH \xrightarrow{Cl_2} \underset{\substack{\text{Monochloro-}\\ \text{acetic acid}}}{CH_2Cl.COOH} \xrightarrow{Cl_2} \underset{\substack{\text{Dichloro-}\\ \text{acetic acid}}}{CHCl_2.COOH} \xrightarrow{Cl_2} \underset{\substack{\text{Trichloro-}\\ \text{acetic acid.}}}{CCl_3.COOH}$$

(vi) Acetic acid has no reducing properties. It does not reduce silver nitrate or mercuric chloride solution (distinction from formic acid). If pure, it does not reduce potassium permanganate solution though the impure acid, perhaps, does.

Acetates.—Salts of acetic acid i.e., acetates are all soluble in water. Sodium acetate is used in the preparation of methane in the laboratory. $CH_3.COONa + NaOH \rightarrow CH_4 + Na_2CO_3$.

Calcium acetate yields acetone on dry distillation.

$$\left.\begin{matrix} CH_3.COO \\ CH_3.COO \end{matrix}\right> Ca \rightarrow CaCO_3 + CH_3.CO.CH_3.$$

Basic copper acetate (verdigris) is an important green pigment.

Ferric acetate and aluminium acetate are used as mordants (fixing agents) in dyeing.

Ammonium acetate when heated gives acetamide.

$$CH_3.COONH_4 = CH_3.CONH_2 + H_2O.$$

Basic lead acetate is used under the name of 'Goulard lotion' for the treatment of sprains.

Tests.—(1) Ferric chloride gives a blood red coloration when it is added to a neutral solution of an acetate.

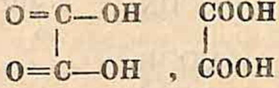
(2) When acetic acid or an acetate is heated with ethyl alcohol and concentrated sulphuric acid, the sweet odour of ethyl acetate is obtained.

(3) Acetic acid itself may be recognised by its vinegar-like odour.

(4) Acetic acid or an acetate does not reduce silver nitrate or mercuric chloride solution even on warming.

Uses.—Acetic acid is used as a solvent. It is also used for the preparation of white lead, acetone, ethyl acetate, cellulose acetate (artificial silk) etc.

Oxalic acid,



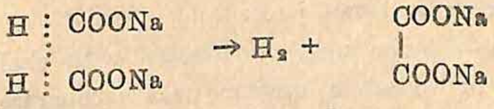
$$\begin{array}{l} O=C-OH \\ \quad\ | \\ O=C-OH \end{array} , \begin{array}{c} COOH \\ | \\ COOH \end{array}$$

Oxalic acid is found in many plants belonging to the family of oxalis. Hence, the name, oxalic acid.

Laboratory Preparation.—Oxalic acid is obtained in the laboratory by oxidising cane sugar (25 gms.) with conc. nitric acid (200 c.c.). At first the cane sugar is heated on a water bath with 50 c.c. of concentrated nitric acid. Torrents of nitrogen peroxide are given out. The preparation is therefore done within a fume chamber. When the reaction subsides, the remaining 150 c.c. of nitric acid are added in lots of 25 c.c. each, fresh addition being made when the reaction due to the previous one has subsided. The solution is then concentrated to a small bulk when on cooling, crystals of oxalic acid are obtained.

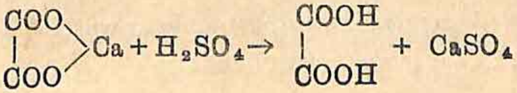
Manufacture :—

(1) On a large scale, oxalic acid is obtained by heating sodium formate rapidly at 400°C when sodium oxalate is formed.



$$\begin{array}{l} H \vdots COONa \\ \ \ \vdots \\ H \vdots COONa \end{array} \rightarrow H_2 + \begin{array}{c} COONa \\ | \\ COONa \end{array}$$

The sodium oxalate produced is first converted into insoluble calcium oxalate and the latter is then decomposed by dilute sulphuric acid.



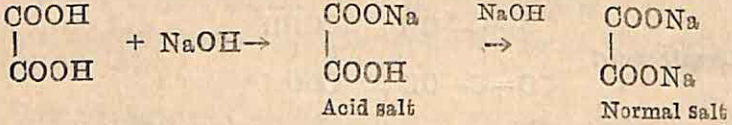
$$\begin{array}{l} COO \\ | \\ COO \end{array}\!\!>Ca + H_2SO_4 \rightarrow \begin{array}{c} COOH \\ | \\ COOH \end{array} + CaSO_4$$

Calcium sulphate is filtered off and the filtrate is evaporated to a small bulk when crystals of oxalic acid, $\begin{array}{l}COOH\\ |\\ COOH\end{array}$, $2H_2O$ are obtained on cooling.

(2) Oxalic acid can be obtained by carefully heating a paste of sawdust with a mixture of caustic soda and caustic potash on an iron tray at about 250°C. The melt contains alkali oxalates from which crystals of oxalic acid are obtained as described above.

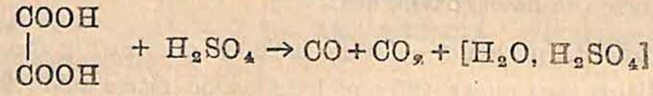
Properties.—Oxalic acid crystallises with two molecules of water. It is soluble in water. Its calcium salt is insoluble in water. It is poisonous.

Being a dibasic acid, it forms normal and acid salts.



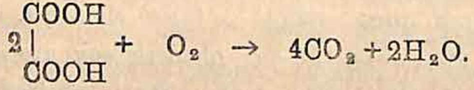
$$\begin{array}{l}COOH\\ |\\ COOH\end{array} + NaOH \rightarrow \underset{\text{Acid salt}}{\begin{array}{l}COONa\\ |\\ COOH\end{array}} \xrightarrow{NaOH} \underset{\text{Normal salt}}{\begin{array}{l}COONa\\ |\\ COONa\end{array}}$$

It is decomposed by conc. sulphuric acid.



$$\begin{array}{l}COOH\\ |\\ COOH\end{array} + H_2SO_4 \rightarrow CO + CO_2 + [H_2O, H_2SO_4]$$

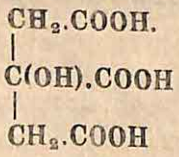
It is oxidised by hot acidified $KMnO_4$ solution completely into $CO_2 + H_2O$



$$2\begin{array}{l}COOH\\ |\\ COOH\end{array} + O_2 \rightarrow 4CO_2 + 2H_2O.$$

Uses.—Oxalic acid is used in chemical analysis, in metal polish and for removing ink-stains.

Citric acid,



$$\begin{array}{l}CH_2.COOH.\\ |\\ C(OH).COOH\\ |\\ CH_2.COOH\end{array}$$

Citric acid occurs in lemon juice.

Preparation.—Lemon juice is neutralised with chalk and filtered. The filtrate is boiled when calcium citrate being less soluble in hot water than in cold water is thrown down. Calcium citrate is now decomposed by sulphuric acid. $CaSO_4$ is filtered off and the solution is crystallised, when citric acid crystals are obtained.

Citric acid is a crystalline solid soluble in water. It is a tribasic acid and hence it forms three series of salts.

Its calcium salt is less soluble in hot water than in cold water.

Uses.—Citric acid is used in the preparation of lemonades and other cold drinks. Sodium citrate is used in medicine.

Exercise.

1. Write down the structural formula of the following :—

(*a*) benzene, (*b*) naphthalene, (*c*) oxalic acid, (*d*) toluene, (*e*) citric acid and (*f*) acetaldehyde.

2. Write down the formulae of a (*a*) monobasic, (*b*) dibasic and (*c*) tribasic organic acid ? How can you distinguish between them ?

3. Describe the preparation of acetic acid from pyroligneous acid, and also from acetylene. Describe its important properties and uses.

4. How is oxalic acid prepared on a large scale ? What is the action of (*a*) conc. H_2SO_4 and (*b*) acidified $KMnO_4$ solution on it ?

5. Write short notes on the following :—(*a*) isomerism, (*b*) homologous series, (*c*) structural formula, (*d*) molecular formula, (*e*) fermentation and (*f*) enzyme.

6. What is the natural source of citric acid ? How is it prepared ? State its important properties and uses.

7. Describe with equations the preparation of the following : (*a*) Acetic acid from ethyl alcohol ; (*b*) Acetaldehyde from ethyl alcohol ; (*c*) Chloroform from ethyl alcohol ; (*d*) Benzene from benzoic acid. *Cal. Pre-U., 1961.*

8. Write the formula of acetic, oxalic and citric acids. How is acetic acid prepared ? Describe its properties and uses. *Cal. Pre-U., 1964.*

9. What is the natural source of citric acid ? Describe how citric acid is prepared. *Cal. Pre-U., 1965.*

CHAPTER L

ESTERS

Ethyl Acetate, $CH_3.COO.C_2H_5$

An ester is a compound formed by replacing the replaceable hydrogen of the acid by an alkyl radical. Ethyl acetate is an ester of acetic acid.

Preparation.—Ethyl acetate is prepared by the action of acetic acid on ethyl alchol in presence of sulphuric acid.

Sulphuric acid acts as a catalyst and helps the prevention of the back reaction by absorbing the water formed in the reaction.

$$CH_3.COOH + HOC_2H_5 \rightarrow CH_3.COO.C_2H_5 + H_2O$$

Experiment.—A distilling flask fitted with a dropping funel, a condenser and a receiver is set up as shown in fig. 127.

A thermometer is introduced into the flask through the cork. 50 c.c. of concentrated sulphuric acid are mixed gradually with 50 c.c. of ethyl alcohol with constant shaking and cooling. The mixture is then placed inside the flask which is heated on an oil bath to 140°C. Through the dropping funnel, a mixture of ethyl alcohol and glacial acetic acid is run in at the same rate at which distillation takes place.

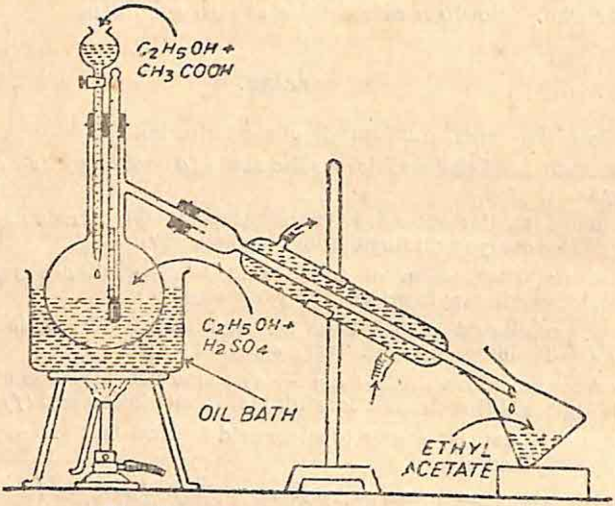


Fig. 127.—Preparation of ethyl acetate.

The distillate is shaken up with a concentrated solution of sodium chloride containing some sodium carbonate when unchanged acetic acid and alcohol go into solution and ethyl acetate separates out as an oily liquid. It is dried over fused calcium chloride and distilled.

Properties.—Ethyl acetate is a colourless, sweet smelling liquid, lighter than water in which it is only slightly soluble. It boils at 77·5°C.

Reaction.—Ethyl acetate is slowly decomposed by water (more rapidly in presence of an alkali) into ethyl alcohol and acetic acid.

$$CH_3.COO.C_2H_5 + H_2O \rightleftharpoons CH_3.COOH + C_2H_5OH$$

Ethyl acetate reacts with ammonia to give acetamide and ethyl alcohol.

$$CH_3.COO.C_2H_5 + HNH_2 \rightarrow \underset{\text{Acetamide}}{CH_3.CO.NH_2} + C_2H_5OH$$

Ethyl acetate can be reduced to ethyl alcohol by sodium and alcohol (Bouveault and Blanc's method) or by hydrogen under pressure in the presence of copper chromite.

$$CH_3.COO.C_2H_5 + 4H \rightarrow 2CH_3.CH_2OH$$

Uses.—Ethyl acetate is used as a solvent. Esters generally have fruity odours. Many of them, therefore, are used for making artificial fruit essences.

Esters of mineral acids are easier to prepare. No catalyst is generally required, because the mineral acids are strong enough to catalyse their own esterification.

Exercise.

1. What is an ester? Name and give the structural formula of an ester. Describe its preparation, properties and uses.

2. Describe with equations what happens when :—

(*a*) $CH_3.COO.C_2H_5$ is heated with alkali.

(*b*) $C_2H_5.OH$ is treated with Iodine in presence of alkali.

(*c*) Benzene is gently heated with concentrated nitric acid in the presence of concentrated sulphuric acid.

(*d*) 'Dry' calcium acetate is heated. *Cal. Pre-U., 1964.*

CHAPTER LI

FUEL GASES

In an earlier chapter, we have read about coal gas—its production and uses (See chapter XX). It is an example of a fuel gas—a mixture of inflammable gases used for the production of heat and light. There are many other kinds of fuel gases used in industry and in homes of people (See below). Fuel gases have many advantages over conventional solid fuels, such as wood, coke, charcoal etc. Fuel gases burn completely giving rise to little or no smoke. They can be easily distributed to consumers through pipes or in cylinders. In contrast, solid fuels burn incompletely and hence produce much smoke which finding its way into the air fouls it endangering the health of the locality. Smoke is one of the banes of modern city life. People are therefore, taking more and more to fuel gases for domestic and industrial purposes.

Though a bit costlier than solid fuels, it is much superior to the latter in point of cleanliness, health and calorific value. Fuel gases again, may be used to heat objects such as cylinders of gas engines which are beyond the reach of solid fuels.

Fuel Gas	Composition Per centage by volume	Heat of combustion B. t. u. per cu. ft. (*1 K. cal.* = 3·968 *B.t.u.*)
Coal gas coke oven gas	CO 6·3, CO_2 1·8, H_2 53, CH_4 31 C_2H_6 3·7, N_2 3·5, O_2 0·2, Illuminants 3·7	500–600
Natural gas	CH_4 85, C_2H_6 9, remainder higher paraffins, N_2, O_2 etc.	900–1300
Producer gas	CO 30, H_2 10·5, CH_4 1·5, CO_2 3, N_2 54·5, O_2 0·5	100–175
Water gas	CO 43, CO_2 4, H_2 48, CH_4 8, O_2 0·8, N_2 3·2	250–325
Carburetted Water gas	CO 34, CO_2 3, H_2 41 N_2 2·5, O_2 0·5, CH_4 10 remainder illuminants 9.	500–550

Composition :

All fuel gases are mixtures of carbon monoxide, hydrogen and hydrocarbons containing one to two carbon atoms. Small amounts of higher hydrocarbons may also be present but their presence is incidental and undesirable. Besides these, some non-inflammable gases are also present as diluents. A small quantity of objectionable impurities may also occur in spite of careful methods of purification.

Technique of Fuel gas production

Except natural gas, the other fuel gases are obtained from solid and liquid fuels. The technology of fuel gas manufacture consists in converting the large complex molecules of carbonaceous solid and liquid fuels into simpler molecules containing one or two carbon atoms in union with hydrogen (or oxygen).

The basic actions of these processes consist of :

(1) *Destructive distillation of* coal, wood etc. (See p. 222 & p. 314)

(2) *Cracking or pyrolysis*, that is, the thermal decomposition of large hydrocarbon molecules of mineral oils.

(3) *Reaction with steam* at high temperatures as in the production of water gas.

(4) *Partial oxidation* as in the production of producer gas by the partial oxidation of coke or charcoal.

(5) *Bacterial fermentation* as in the production of sewage gas.

Individual Fuel Gases

(1) Natural gas :

In many parts of world, particularly in America and Russia, inflammable gases are found to issue from the crevices of the earth's surface. They often catch fire and burn continuously. Such eternal fires situated near lake Baku used to draw fire worshippers from all over the world. Inflammable gases also issue from the heads of oil wells. Sometimes, huge deposits of gases are discovered while digging wells for oil. Such wells (called dry wells) contain no oil but only gases. The large quantities of gases found associated or disassociated with liquid petroleum are known as *natural gas*.

More than eighty per cent of natural gas is composed of methane. Higher paraffins occur in decreasing proportions.

Natural gas is used as a domestic and industrial fuel. Apart from its use as a fuel it finds application in the manufacture of carbon black, methyl alcohol etc.

(2) Producer gas :

It is essentially a mixture of carbon monoxide and nitrogen produced by passing air through a bed of red hot coke. The gas is manufactured in a closed air-tight cylindrical vessel called a *producer*. The producer is made of wrought iron sheets lined inside with fire bricks. There is an outlet for the producer gas near the top (see fig. 128).

The producer is fed with coke by means of a device at the top which enables the operation to be done without admitting much unwanted air. There are fire-bars at the bottom on which the coke rests. Air is blown in through the hole at the bottom. At first coke burns to carbon dioxide, but as it ascends through the layers of red hot coke, it is reduced to carbon monoxide.

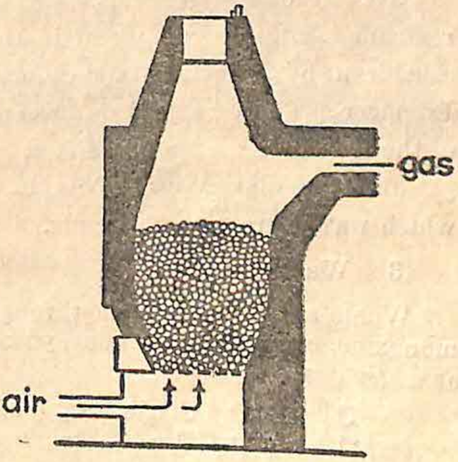


Fig. 128—Manf. of Producer gas.

$C + O_2 = CO_2$ ...(1)
$CO_2 + C \rightleftharpoons 2CO$...(2)

The second reaction being reversible, some CO_2 is always present. The ratio CO/CO_2 in the gas increases as the temperature is raised.

The maximum proportion of carbon monoxide is produced at about 1000°C and almost nil at or below 450°C. Hence, the temperature in the producer should be in the neighbourhood of 1000°C.

The conversion of coke to producer gas is an exothermic reaction (29 K. cal. per gm. molecule of carbon). An additional quantity of heat (68 K. cal.) is produced when the gas produced from the same quantity of carbon is burnt to carbon dioxide.

It is, therefore, evident that unless the gas is burnt when still hot, the entire heat evolved in the production of producer gas is lost. Hence, and also because of the low calorific value, it does not pay to distribute the gas.

The producer gas must therefore be used on or near the very spot where it is produced.

A furnace using producer gas as fuel is built in two parts, the producer and the combustion chamber by its side. In the former only as much air is introduced as is necessary to oxidise carbon to carbon monoxide. In the latter, secondary air is admitted to burn the carbon monoxide to carbon dioxide. If the gas is to be used in a gas engine, it should be washed free of dust particles and ash. Although this means the loss of that portion of heat which is produced when coke is converted into producer gas, nevertheless, this has to be done to prevent damage to gas engine cylinders.

Use.—Producer gas is used as a fuel in industry and also as a reducing agent, for example, it is used in the manufacture of steel from cast iron by Siemen Martin Open Hearth process (see page 299). Producer gas may be used in place of petrol in times of acute shortage of the latter. As a matter of fact, motor vehicles were run on producer gas during the last World War in India in order to economise petrol which was in great short supply.

(3) Water gas :

When steam is passed through red hot coke, a mixture of carbon monoxide, carbon dioxide and hydrogen is produced, which is known as *water gas*.

$$C + 2H_2O = CO_2 + 2H_2 \text{ (\textit{dull red heat})}$$
$$C + H_2O = CO + H_2 \text{ (\textit{bright red heat})}$$

Both the reactions are endothermic. Hence with time, the temperature of the red hot coke falls With the decrease of temperature, the proportion of carbon dioxide in the gas mixture increases. Hence, after, say, about 8 minutes, the supply of steam is stopped and in its stead air is passed for a period of about 2 minutes in order to raise the temperature of the coke to bright redness again. The gas produced (CO and N_2) during the passage of air is allowed to escape and again steam is turned on. Thus steam and air are passed alternately to keep up the temperature of the furnace.

(4) Semi Water gas :

If the two operations are combined, that is, if steam along with a small quantity of air just sufficient to maintain the temperature of the furnace is passed, a mixture of gases is produced which contains nitrogen and a larger proportion of carbon monoxide than is present in water gas in addition to hydrogen. It is called *a semi water gas.*

(5) Carburetted water gas :

Water gas burns with a non-luminous flame. Hence, though very useful as a heating agent it cannot be used as an illuminating agent unless a mantle is used in conjunction with it. Hence, it is mixed with gaseous hydrocarbons (obtained by the cracking of oil) to make it burn with a luminous flame. Water gas so treated is called *carburetted water gas.*

(6) Oil gas :

In Moffussil towns, where there is no coal gas supply, oil gas is used in the laboratories instead of coal gas. The gas is prepared by dropping crude oil (sometimes kerosene oil) into retorts heated to bright redness. The complex and large molecules of hydrocarbons which are the constituents of the oil break up at the high temperature yielding simpler molecules of gaseous hydrocarbons. The gases are cooled when some tar separates. The uncondensed gases are washed and then stored up in gas-holders.

Exercise.

1. Name some common fuel gases and state the advantages of fuel gases over solid fuels in industry as well as for domestic purposes.

2. Describe the composition of important fuel gases and the technique of their preparation.

3. What is producer gas ? How is it prepared ? State its chief uses in industry.

CHAPTER LII

CHEMICAL CALCULATIONS

CALCULATIONS DEPENDING UPON CHEMICAL EQUATIONS

A. Calculations involving Weight and Weight.

When the equation representing a chemical reaction is known, it is always possible to calculate either the weights of substances produced from the given weights of the materials used, or the weights of the materials required to produce the given weights of the substances. Thus from the equation—

$$\underset{32}{S} \quad + \quad \underset{32}{O_2} \quad = \quad \underset{64}{SO_2}$$

we find that we can calculate either (i) the weight of sulphur dioxide produced by the chemical reaction taking place between 32 gms. of sulphur and 32 gms. of oxygen; or (ii) the weight of sulphur and oxygen required to produce 64 gms. of sulphur dioxide.

The weights are *relative*. They hold true whatever units are used. Thus from the above equation it will be *equally* correct to say that—

32 pounds of sulphur combine with 32 pounds of oxygen to produce 64 pounds of sulphur dioxide Or, 32 maunds of sulphur combine with 32 maunds of oxygen to produce 64 maunds of sulphur dioxide.

Method.—First write out the equation correctly representing the chemical reaction. Now note down the relative weights of the substances below their formulae, remembering that the molecular weight is obtained by adding together the atomic weights.

Problems

1. *Find the weight of quicklime obtained by strongly heating 10 gms. of marble.* $Ca=40$, $C=12$, $O=16$.

$$\underset{\substack{(40+12+48)\\100}}{CaCO_3} \quad = \quad \underset{\substack{(40+16)\\56}}{CaO} \quad + \quad CO_2$$

100 gms. of marble on being strongly heated yield 56 gms. of quicklime.

$\therefore$ 10 gms. of marble will yield $\frac{10\times 56}{100}=5{\cdot}6$ gms. of quicklime.

2. *An impure sample of soda ash contains 68 per cent of sodium carbonate. Find the weight of soda ash required to prepare 20 seers of caustic soda.*

$$\underset{106}{Na_2CO_3} + Ca(OH)_2 = CaCO_3 + \underset{80}{2NaOH}$$

80 *seers* of NaOH are obtained from 106 *seers* of soda carb.

$\therefore$ 20 *seers* of NaOH will be obtd. from $\frac{20\times 106}{80}=26{\cdot}5$ *seers* of soda carb.

But 68 *seers* of soda carb. are present in 100 *seers* of soda ash.

Hence, 26·5 *seers* of soda carb. will be present in $\frac{26·5 \times 100}{68}$

$= 38·97$ *seers of soda ash.*

3. *A solution of nitric acid of specific gravity 1·46 contains 60 per cent HNO_3. What weight of this solution is theoretically required to dissolve 5 grams of cupric oxide ?*

$$\underset{79·5}{CuO} + \underset{2\times 63}{2HNO_3} = Cu(NO_3)_2 + H_2O$$

79·5 gms. of CuO require 2×63 gms. of HNO_3.

∴ 5 gms. of CuO will require $(5 \times 2 \times 63) \div 79·5$ gms. of HNO_3.

Now 60 gms. of the acid are present in 100 c.c. of the sol.

∴ $(5 \times 2 \times 63) \div 79·5$ gms. of HNO_3 will be present in

$$\left(\frac{5 \times 2 \times 63 \times 100}{60 \times 79·5}\right) \text{ c.c. of } HNO_3 \text{ sol.}$$

And the sp. gr. of HNO_3 being 1·46, the weight of this vol. of nitric acid sol. will be

$$\left(\frac{5 \times 2 \times 63 \times 100 \times 1·46}{60 \times 79·5}\right) = 19·28 \text{ gms.}$$

Exercise.

1. How much $KClO_3$ would you take to prepare 5 grams of oxygen ? (*C. U. 1892*) **[Ans. = 12·76 gms.]**

2. Calculate the weight of zinc required to liberate 100 gms. of hydrogen from sulphuric acid. **[Ans. = 32·50 gms. of Zn.]**

3. What is the wt. of iron which is converted into its oxide by the action of 18 gms. of steam ? **[Ans. = 42 gms.]**

4. 24 seers of oxygen are reacted with 4 seers of hydrogen. How much water is produced ? Would either of the elements be in excess ? If so, calculate its weight. **[Ans. H_2O = 57 gms. H_2 in excess, its wt. = 1 gm.]**

5. How much nitre (KNO_3) will be required to produce sufficient nitric acid to dissolve 50 gms. of Cu ? **[Ans. = 212·07 gms.]**

6. A box of washing soda (Na_2CO_3, $10H_2O$) weighs 30 seers when packed. What is the least weight it can have due to loss of moisture only ? **[Ans. = 11·12 seers.]**

7. What weight of H_2SO_4 can theoretically be obtained from 500 tons of pyrities containing 48 p. c. of sulphur ? **[Ans. = 735 tons.]**

8. How much $KClO_3$ must be heated to yield as much oxygen as would be obtained from 500 gms. of HgO ? **[Ans. = 94·52 gms.]**

9. 1·4 gms. of copper are displaced from a solution of copper sulphate in water by iron. Find the wt. of ferrous sulphate produced. **[Ans. = 3·351 gms.]**

10. One litre of sodium chloride solution (sp. gr. 1·08) containing 2·64% of sod. chloride, NaCl, is evaporated to dryness. What weight of chlorine can be obtained by heating it with MnO_2 and H_2SO_4 ?

11. 24·5 grams of $KClO_3$ are heated to produce oxygen. Hydrogen is generated by the action of dilute sulphuric acid on zinc. What weight of zinc will be required to produce just sufficient hydrogen to completely combine with the oxygen obtained from the $KClO_3$ (K = 39, Zn = 65, Cl = 35·5). *Cal. Pre-U. 1961.*

12. 1·5 grams of a sample of coal containing 85% of carbon, 5% of hydrogen and 10% of oxygen are completely burnt in dry air free from CO_2 and the products are passed successively through two weighed U-tubes filled respectively with fused $CaCl_2$ and soda lime. Calculate the alterations, if any, in the weights of the U-tubes. *Cal. Pre-U. 1963.*

The Vapour Density of a Gas

The vapour density of a gas means its density relative to hydrogen, i.e. how many times it is heavier than an equal volume of hydrogen measured at the same temperature and pressure.

$$\text{Vapour density} = \frac{\text{wt. of a given vol. of gas}}{\text{wt. of an equal vol. of hydrogen}} \text{ at S. T. P.}$$

If the vapour-density of the gas is to be expressed relative to any other gas, say air or oxygen, it can be done by dividing the vapour density of the gas by that of the other gas with which it is compared. For example, the vapour density of sulphur dioxide relative to air (air = 1) is equal to

$$\frac{\text{Vapour density of } SO_2 \text{ relative to hydrogen}}{\text{Vapour density of air relative to hydrogen}}$$

It is worthwhile to remember that 1 litre of hydrogen at N.T.P. weighs 0·09 gm. and that air is about 14·4 times heavier than an equal volume of hydrogen i.e. its vapour density relative to hydrogen is 14·4.

Example.—*Find the vapour density of a gas, 500 c.c. of which weigh 1·98 gm.*

Weight of 500 c.c. of hydrogen (equal volume) is

$$\frac{0{\cdot}09}{1000} \times 500 \text{ gm.} = \frac{0{\cdot}45}{10} = 0{\cdot}045 \text{ gm.}$$

$$\therefore \quad \text{V.D.} = \frac{1{\cdot}98}{0{\cdot}045} = 44.$$

Absolute density of a gas (mass per unit volume) may be obtained by multiplying the vapour density of the gas by 0·09 as so many gms. per litre. Thus the absolute density of a gas having V. D. = 22 is 22 × 0·09 = 1·98 gms./litre.

Vapour density from molecular formula of a gas.

First find out the mol. wt. of the gas by adding up the At. wts. of all the atoms in the molecule.

Now the V. D. of the gas is obtained by dividing the mol. wt. obtained by two; for we know from Avogadro's hypothesis that vapour density of a gas is half its mol. wt.

To calculate the wt. of a given volume of a gas.

This can be done in two ways :

Method No. 1. First determine the vapour density of the gas from the molecular formula by way of mol. wt. as shown above. Now determine its absolute density in grams per litre at N.T.P. by multiplying the V. D. by 0·09. The volume in litres multiplied by its absolute density gives the required weight.

Find the wt. of 250 c.c. of carbon dioxide at N.T.P.

Formula of carbon dioxide $= CO_2$

$\therefore$ Mol. wt. $= 12 + 32 = 44$

But V. D. $= \frac{\text{Mol. wt.}}{2} = \frac{44}{2} = 22$

$\therefore$ Absolute density $= 22 \times 0{\cdot}09 = 1{\cdot}98$ gms. per litre.

$\therefore$ 1000 c.c. of CO_2 at N.T.P. weigh 1·98 gms.

$\therefore$ 250 c.c. " " " " " $\frac{1{\cdot}98 \times 250}{1000} = 0{\cdot}495$ gm.

Method No. 2. This is based on the fact that the gm. mol. wt. of any gas (elementary or compound) occupies 22·4 litres at N.T.P.

Example.—*Find the wt. of 2400 c, c. of ammonia gas at N.T.P.*

Mol. formula of Ammonia is NH_3

$\therefore$ Mol. wt. of $NH_3 = 14 + 3 = 17$

Hence, 22·4 litres of NH_3 at N.T.P. weigh 17 gms.

$\therefore$ 2400 c.c. i.e. 2·4 litres of NH_3 weigh $\frac{17 \times 2{\cdot}4}{22{\cdot}4} = 1{\cdot}82$ gms.

Calculation involving Weight and Volume

To calculate the volume of a gas evolved in a chemical reaction.

First write out the equation.

There are again two methods of doing it.

1st. Method. First find out the weight of the gas and then calculate its volume.

2nd. Method. Put down 22·4 litres for each molecule of the gas in the equation the weights being expressed in grams as before.

N. B. *Such volume calculations apply to the case of gases only and not to solids and liquids. Volumes of gases obtained are at N.T.P. If volumes are wanted at any other temps. and pressures, they must be so converted by means of Charles' and Boyle's law.*

Examples.

1. *What volume of oxygen collected at standard temp. and pressure is given off on heating 1 gram of mercuric oxide ?*

$$\underset{2\,(200+16)=432}{2HgO} = 2Hg + \underset{32}{O_2}$$

432 gms. of mercuric oxide yield 32 gms. of oxygen.

∴ 1 gm. of HgO will yield $\left(\frac{32\times 1}{432}\right)=0{\cdot}074$ gm. of oxygen.

Now, 32 gms. of Oxygen occupy 22·4 litres at N.T.P. Therefore, 0·074 gm. of Oxygen will occupy

$$32 : 0{\cdot}074 :: 22{\cdot}4 : x$$

Or, $x=\left(\frac{0{\cdot}074\times 22{\cdot}4}{32}\right)=0{\cdot}0518$ litre at N.T.P.

Alternative method—

$$\underset{2(200+16)\text{ gms.}}{2HgO} = 2Hg + \underset{22{\cdot}4\text{ litres}}{O_2}$$

432 gms. of mercuric oxide yield 22·4 litres of oxygen at N.T.P.

∴ 1 gm. of HgO will yield $\left(\frac{1\times 22{\cdot}4}{432}\right)=0{\cdot}0518$ litre at N.T.P.

2. *What weight of sulphur must be burnt in air so as to yield 10 litres of sulphur dioxide at standard temperature and pressure ?*

$$\underset{32\text{ gms.}}{S} + O_2 = \underset{22{\cdot}4\text{ litres at N.T.P.}}{SO_2}$$

Here we see that 22·4 litres of SO_2 at N.T.P. will be obtained by burning 32 gms. of sulphur.

∴ 10 litres of sulphur dioxide at N.T.P. will be obtained by burning,

$$22{\cdot}4 : 10 :: 32 : x$$

Or, $x=(10\times 32)\div 22{\cdot}4=14{\cdot}28$ gms. of sulphur.

3. *2·5 litres of nitrous oxide have been collected at 39°C and 741 mm. pressure. What weight of ammonium nitrate must have been decomposed for the purpose ?*

Let 2·5 litres of nitrous oxide occupy V litres at N.T.P.

∴ $\frac{2{\cdot}5\times 741}{39\times 273}=\frac{V\times 760}{273}$. Or, $V=\frac{2{\cdot}5\times 741\times 273}{760\times 312}$ litres

Now, from the equation—

$$\underset{(14+4+14+48)\text{ gms.}}{NH_4NO_3} = \underset{22{\cdot}4\text{ litres}}{N_2O} + 2H_2O$$

22·4 litres of nitrous oxide at N. T. P. are obtained from 80 gms. of ammonium nitrate.

∴ V litres of nitrous oxide will be obtained from

$\left(\frac{2{\cdot}5\times 741\times 273}{760\times 312}\times\frac{80}{22{\cdot}4}\right)=7{\cdot}617$ gms. of ammonium nitrate.

Exercise.

1. Find the weights of 200 c.c. at N.T.P. of (*a*) ammonia, (*b*) nitrous oxide, (*c*) chlorine and (*d*) nitrogen. Find their vapour densities relative to oxygen.

2. Find the wt. of 6 litres of hydrogen at 32°F and 760 mm. *Madras.* **[Ans.=0·54 gms.]**

3. What weight of NH_4Cl would be required to prepare 10 litres of ammonia at N. T, P. ? *C. U. 1902.* **[Ans.=23·38 gms.]**

4. What volume of oxygen at 12°C and 780 mm. will be required to burn all the hydrogen evolved by the action of dil. HCl on 25 gms. of zinc ? ($Zn=65$) *C. U. 1908.* **[Ans.=4·37 litres.]**

5. 100 gms of KNO_3 are heated to redness ; what volume of oxygen at 39°C and 765 mm. pressure is evolved ? *All. 1931,* **[Ans.=12·59 litres]**

6. What weight of alcohol (C_2H_6O) should yield 2 litres of ethylene (C_2H_4) at 15°C and 750 mm. pressure ? **[Ans.=3·84 gms.]**

7. Calculate the wt. of iron converted into oxide by the action of 18 gms. to steam and find the volume of hydrogen at N.T.P. produced. *C. U. 1904.* **[Ans. Fe=42 gms, H=22·4 litres.]**

8. What volume of oxygen is obtained at 94·5°C and under 669 mm. pressure from 91 gms. of $KClO_3$, being given that the gram-molecular wt. of any gas occupies 22·4 litres an N,T.P. ? **[Ans.=38 litres.]**

9. A balloon of 1000 litres' capacity is to be filled with hydrogen at 27°C and 750 mm. What is the *minimum* quantity of iron required to liberate the necessary amount of hydrogen ? *C. U. 1925.* **[Ans =1683·745 gms.]**

10. Given 100 gms. of chalk, how many litres of CO_2 can be obtained at 15°C and 740 mm. pressure by dissolving the substance in an acid ? *Pat,, 1906, '24.* **[Ans.=24·269 litres.]**

11. One gm. of sodium amalgam. on being treated with water, yields 200 c.c. of hydrogen at 18°C and 76 cm. Find the percentage of sodium in the amalgam. *All.,* **[Ans.=39·2%]**

12. One gm. of a mixture of $CaCO_3$ and $MgCO_3$ gives 240 c.c. of CO_2 at N.T.P. Calculate the composition of the mixture. *Nag.,* **[Ans.=62·5% $CaCO_3$. 37·5% $MgCO_3$]**

Calculations involving volumes of reacting gases and their gaseous products

These problems can be calculated with the help of the Avogadro's hypothesis. It easily follows from the converse of the Avogadro's hypothesis that the ratio between the number of molecules of different gases is also the ratio of their volumes provided that volumes are all measured at the same temperature and pressure.

Examples :—

1. *10 c.c. of oxygen are mixed with 50 c.c. of hydrogen, both measured at N.T.P. and exploded. What volume, if any, of gas will remain ?*

$$\underset{2\ \text{vols.}}{2H_2} + \underset{1\ \text{vol.}}{O_2} = 2H_2O$$

2 c.c. of hydrogen combine with 1 c.c. of oxygen to form water.

∴ 20 c.c. of hydrogen will combine with 10 c.c. of oxygen. Hence there will be left $(50-20)=30$ c.c. of hydrogen unacted upon.

2. *10 c. c. of ethylene are mixed with 40 c. c. of oxygen, both measured at N. T. P. and exploded. Find the nature and volume of gases that will remain at the standard temp. and pressure.*

$$\underset{\text{1 vol.}}{C_2H_4} + \underset{\text{3 vols.}}{3O_2} = \underset{\text{2 vols.}}{2CO_2} + 2H_2O$$

1 vol. of ethylene requires 3 vols. of oxygen to produce 2 vols. of CO_2.

$\therefore$ 10 c.c. of C_2H_4 will require 30 c.c. of oxygen to give 20 c.c. of CO_2.

Hence, the residual gas will be a mixture of $\begin{cases} CO_2 = 20 \text{ c.c.} \\ O_2 = (40 - 30) = 10 \text{c.c.} \end{cases}$

Exercise.

1. What vol. of CO can be obtained theoretically from 100 litres of CO_2, both measured under standard conditions of temp. and pressure?
C. U. 1931. [Ans. = **200 litres.**]

2. 40 c.c. of a mixture of CO and C_2H_2 gases were mixed with 100 c.c. of oxygen in a eudiometer and fired. After cooling, the residual gas occupied 104 c.c. and after treatment with potash the residual gas occupied 48 c.c. Find the composition of the original mixture. *All. 1915.* [Ans. **$CO = 60$ p.c ; $C_2H_2 = 40$ p.c.**]

3. A mixture of 15 c.c. of oxygen, 25 c.c. of hydrogen, 15 c.c. of marsh gas and 10 c.c. of carbon monoxide is taken in a eudiometer tube and exploded. Find out the volume and composition of the residual gas.
[Ans. **Vol. = 27·5 c.c.** and **Comp. $O = 2·5$ c.c. ; $CO_2 = 25$ c.c.**]

4. What vol. of air would be required for the complete combustion of 100 litres of gas containing hydrogen 46, marsh gas 40 and ethylene gas 14 per cent. by volume? Air contains 21 p.c. by vol. of Oxygen. *London I Sc.* [Ans. **Vol. = 690 47 litres.**]

5. One litre of a gas mixture of CO and CO_2 is found to give 1600 c.c. of CO, both measured under same conditions. Calculate the composition by vol of the gas mixture.
C. U. 1914. [Ans. **$CO = 400$ c.c. $CO_2 = 600$ c.c.**]

6. 70 c.c. of CO are mixed with 28 c.c. of oxygen and exploded. If the resulting mixture is shaken with caustic potash, what vol. of gas will remain and what gas will it be?
Bom. B. Sc. 1910. [Ans. = **15 c.c. CO**]

CHAPTER LIII

CHEMICAL ANALYSIS

Chemical analysis is of two kinds—(*a*) qualitative and (*b*) quantitative. The object of the first is to find out what substances (elements, radicals or compounds) are present; of the second to find out their actual amounts in a given substance.

The two common methods employed in quantitative analysis are:

(1) **Gravimetric analysis**: Here the composition of a given substance is found by direct weighing.

(2) **Volumetric analysis** which enables us to determine the composition of a given substance not by direct weighing, but by *titrations* with a *standard solution* with the help of an *indicator* (see below).

Volumetric Analysis : Acidimetry and alkalimetry

Standard Solution.—*By a standard solution we mean a solution of known strength i.e., a solution which contains a known weight of the solute present in a known volume of it.*

Titration—*The operation of determining the strength of an unknown solution by allowing it to react with the standard solution, is called Titration.*

Indicators.—*Indicators are chemicals used in volumetric analysis which indicate, by change of colour, the terminations (i.e., end point) of a chemical reaction.*

The indicator also indicates by change of colour whether a solution is acidic, alkaline or neutral.

The indicators themselves are *weak bases.* Some of them like *litmus, turmeric,* etc. are of vegetable origin. Others like phenolphthalein, methyl orange, etc. are prepared synthetically. The indicator itself *should* not interfere with the reaction.

The following indicators are usually employed :

Indicator.	*Colour in neutral sol.*	*Colour with acids.*	*Colour with alkalis.*
1. Litmus solution	*Purple or Violet*	*Red*	*Blue*
2. Methyl orange	*Orange*	*Pink or red*	*Yellow*
3. Phenolphthalein.	*Colourless*	*Colourless*	*Pink*

Neutralisation : When a solution of an acid is mixed with a solution of an alkali in such proportions (one eq. wt. of one with eq. wt. of the other) that after the reaction between them is over, the solution does not contain any excess of the either (the products of the reaction being a salt and water only), then, the process is known as **Neutralisation.**

$$NaOH + HCl = NaCl + H_2O$$

According to ionic theory, neutralisation means merely the combination of the hydrogen ions furnished by an acid with the hydroxyl ions furnished by an alkali to produce undissociated molecules of water.

In the ionic form, the above equation may be shown as follows :

$$Na^+ + OH^- + H^+ + Cl^- = Na^+ + Cl^- + H_2O$$

Or cancelling common ions (Na^+ and Cl^- ions) on both sides, we have,

$$H^+ + OH^- = H_2O$$

Acidimetry and Alkalimetry.—The strength of an acid may be determined by neutralising it, in presence of an indicator, with an alkali of *known strength* (—*Acidimetry*). Similarly, the strength of an alkali may be determined by neutralising it, in presence of an indicator, with an acid of *known strength* (—*Alkalimetry*).

The key to the clear understanding of the problems in volumetric analysis is a proper grasp of the meaning of the term gram equivalent. Consider the equations.

$$\begin{array}{ccccccccc} NaOH & + & HCl & = & NaCl & + & H_2O \ldots(1) \\ 40 & & 36{\cdot}5 & & 58{\cdot}5 & & 18 \\ 2NaOH & + & H_2SO_4 & = & Na_2SO_4 & + & 2H_2O \ldots(2) \\ 80 & & 98 & & 142 & & 56 \end{array}$$

From the equation (1) we see that *one* gm. mol. wt. (36·5 gms.) of hydrochloric acid neutralises one gm. mol. wt. of caustic soda (40 gms.), whereas we find from equation (2) that the same weight of caustic soda (40 gms.) is neutralised by *half* the gm. mol. wt. (49 gms.) of sulphuric acid.

36·5 gms. of HCl and 49 gms. of H_2SO_4 have one thing common between them, i.e., they each contain 1 gm. of replaceable hydrogen and are known respectively as their gram equivalent weights, for so far as their capacity of neutralising alkalis are concerned, they are equivalent, each separately neutralising 40 gms. of NaOH.

The gram equivalent of an acid may therefore, be defined as the wt. in gm. of the acid which contains 1 gm. of replaceable hydrogen.

$$\text{Gm. eq. wt. of acid} = \frac{\text{Mol. wt. of the acid}}{\text{No. of replaceable hydrogen atoms.}}$$

For example, the gm. eq. wt. of phosphoric acid, H_3PO_4 is found thus. Its gm. mol. wt. $= (3 + 31 + 64)$ gms. $= 98$ gms. No of replaceable hydrogen atoms in its molecule $= 3$.

Hence, gm. eq. wt. of Phosphoric acid $= \frac{98}{3} = 32{\cdot}67$ gms.

The gm. eq. wt. of an alkali is that wt. of an alkali which will just neutralise one gm. eq. wt. of an acid. 40 gms. of NaOH neutralise one gm. eq. wt. of hydrochloric acid (36·5 gms) or one gm. eq. wt. of sulphuric acid (49 gms.)

Hence, gm. eq. wt. of NaOH $= 40$ gms.

Now suppose 40 gms. of NaOH are dissolved in enough water to make one litre of solution and 36·5 gms. of HCl and 49 gms. of H_2SO_4 are also dissolved separately in enough water to make one litre of solution of each.

One litre of the above NaOH solution is mixed separately with one litre of the HCl and with one litre of H_2SO_4 solution as prepared above.

From what has been discussed before, it will be easily seen that in each case complete neutralisation will take place. It also follows from above that equal volumes of two or more solutions of acids (or of alkalis) containing each 1 gm. eq. wt (or an aliquot part thereof) are equivalent so far as their capacities to neutralise an alkali (or an acid) is concerned and are said to have the same strength *in terms of normality*. Strength in terms of normality, therefore, means the number of gm. eq. wts. of solute (acid or alkali) present in one litre of the solution.

Normal solution *of a substance is defined as a solution, a litre of which contains one gram equivalent weight of the substance.* Solutions having concentration higher or lower than normal are used frequently in volumetric analysis. Such concentrations are expressed as follows :—

(6N) HCl means a solution which is six times as strong as normal HCl and hence contains 6 × 36·5 gms. of HCl per litre.

Similarly $\frac{N}{10}$ or 0·1 (N) NaOH (decinormal) means a solution which contains one tenth of the gm. eq. wt. (40 gms.) of caustic soda *i.e.*, 4 gms. dissolved per litre of the solution.

The preceeding discussion shows that *equal volumes* of acid and alkali of *same strength* expressed *in terms of normality neutralise each other.*

If one-tenth normal solution is used instead of a normal solution, the former being only $\frac{1}{10}$th strong than the latter, 10 times the volume of the weaker solution will produce the same effect as the stronger solution (normal solution). In other words, the less the concentration, the more the volume required for a given reaction. In other words, volume and strength are inversely proportional.

$$\frac{V_1}{V_2} = \frac{S_2}{S_1}$$

$$\text{or,}\quad V_1 \times S_1 = V_2 \times S_2$$

Percentage Strength : Strength of a solution may also be expressed in terms of percentage. Percentage strength means the number of gms. of the solute contained per 100 c.c. of the solution. Thus 4% solution of a substance means that 100 c.c. of its solution contain 4 gms. of the substance. When strengths are expressed in terms of percentage, equal volumes of acids and bases will not necessarily neutralise each other.

Example : *What is the result of mixing of 10 c.c. of 4% NaOH solution with 10 c.c. of 4% HCl solution ? State whether they will* *neutralise completely each other or some quantity of acid or alkali will remain un-neutralised. In the latter case, find the amount of the acid or the alkali, as the case may be, which will remain in excess.*

10 c.c. of 4% NaOH soln. contain 0·4 gm. of NaOH.

Again, 10 c.c. of 4% HCl soln. contain 0·4 gm. of HCl soln.

Now, $\underset{40}{NaOH} + \underset{36 \cdot 5}{HCl} = NaCl + H_2O$.

From the above equation, we see

40 gms. of NaOH require 36·5 gms. of HCl for complete neutralisation.

Or, 4 " " 3·65 gms. of HCl " " "

Hence, 4 − 3·65 = 0·35 gm. of HCl will remain in excess. The solution will be acidic.

This is the reason, why in acidimetry and alkalimetry, the strength of a solution is usually expressed in terms of normality rather than as percentage strength.

Strengths in terms of Gms. per litre :

The strength of a solution in gms. per litre means the number of gms. of the solute present in 1 litre of the solution. It is obtained by multiplying the *normality factor* of a solution by the eq. wt. of the solute (*the normality factor being the fraction of the gm. eq. wt. of any substance contained in 1 litre of its solution.*)

Thus, if the normality factor of a NaOH solution is 0·024, it means that the solution contains 0·024 × 40 gms. of NaOH in 1 litre of its solution.

Some Useful Rules :

(*i*) As the strength of a solution on dilution varies inversely as the volume.

1 c.c. of 2(N) soln. ≡ 2 c.c. of (N) soln.
Or, x c.c. of 2(N) soln. ≡ $2x$ c.c. of (N) soln.

Similarly,

x c.c. of N/2 soln. ≡ $x \times 1/2$ c.c. of (N) soln.
and x c.c. of N/10 soln. ≡ $x \times 1/10$ c.c. of (N) soln.
In general, x c.c. of y (N) soln. ≡ xy c.c. of (N) soln.

(*ii*) Acid and Alkali solns. of same strength in terms of normality neutralise each other in equal volumes.
x c.c. of y (N) acid ≡ x c.c. of y(N) alkali.

(*iii*) Strength of Acid × Vol. of Acid = Strength of Alkali × Vol. of Alkali.
If, V_1 c.c. of (S_1) Acid ≡ V_2 c.c. of (S_2) Alkali.

Then, $V_1 \times S_1 = V_2 \times S_2$ (S_1 and S_2 being the strength of the acid and alkali respectively).

N. B.—The symbol (≡) has been used above to mean *exactly neutralise* or *just react with* or *equivalent to*.

(*iv*) The number of gms. of a substance present in x litre of its y (N) soln.

$= x \times y \times$ eq. wt. of the substance.

Thus, the amount of Na_2CO_3 present in 250 c.c. of N/10 Na_2CO_3 soln. is

$1/4 \times 1/10 \times 53 = 53/40 = 1{\cdot}325$ gms.

(53 being the eq. wt. of Na_2CO_3)

Examples :—

(*1*) *50 c.c. of caustic soda solution exactly neutralise 75 c.c. of* $\frac{N}{3}$ *HCl. Find the strength of caustic soda solution.*

Let the strength of the caustic soda solution be x. Then

$$V_1 \times S_1 = V_2 \times S_2$$

$$\text{Hence,}\quad 50 \times x = 75 \times \frac{N}{3}$$

$$\text{or,}\quad x = \frac{75 \times N}{50 \times 3} = \frac{N}{2}$$

(2) *20 c.c. of a solution of* Na_2CO_3 *in water required 8·2 c.c. of* (*N/10*) *HCl for complete neutralisation. Find the strength of* Na_2CO_3 *soln.*—(*a*) *in terms of normality, and* (*b*) *wt. in gms. present in a litre.*

(*a*) Let the strength of Na_2CO_3 sol. be x.

Since $V_1 \times S_1 = V_2 \times S_2$.

$20 \times x = 8{\cdot}2 \times (N/10) \equiv 0{\cdot}82$ (N)

or, $x = (0{\cdot}82 \div 20)$ (N) $= 0{\cdot}041$ (N)

∴ The strength of Na_2CO_3 sol. is 0·041 (N)

(*b*) 1000 c.c. of (N) Na_2CO_3 sol. contain 53 gms. of Na_2CO_3.

∴ 1000 c.c. of 0·041 (N) Na_2CO_3 sol. contain

$(53 \times 0{\cdot}041) = 2{\cdot}173$ gms, of Na_2CO_3. [*Rule* (*i*)]

(*3*) *One gram of sodium hydroxide was dissolved in 50 c.c. of normal hydrochloric acid solution. How many c.c. of normal solution of sodium hydroxide will be needed to make the solution neutral ?*

Cal. Pre-U., 1961.

50 c.c. of (N) HCl ≡ 50 c.c. of (N) NaOH.

$= \frac{50}{1000} \times 40 = 2$ gms. of NaOH (*Rule iv*)

Hence, 50 c.c. of (N) HCl require 2 gms. of NaOH for neutralisation.

But only 1 gm. of NaOH was dissolved in 50 c.c. of (N) HCl.

Therefore, another 1 gm. of NaOH will be reqd. for neutralisation.

But, 1 gm. of NaOH is present in $\frac{1000}{40}$ c.c. $=25$ c.c. of (N) NaOH soln.

Hence, 25 c.c. of (N) NaOH soln. will be needed.

(4) *0·125 gram of anhydrous sodium carbonate was dissolved in water and it was found that 248 c.c. of a solution of sulphuric acid were required to neutralise it exactly. Calculate (a) the normality of the acid and (b) the weight of sulphuric acid present in one litre. (Na=23)* *Cal. Pre-U., 1962.*

5·3 gms. of Na_2CO_3 are present in 1000 c.c. of $\left(\frac{N}{10}\right)$ Na_2CO_3.

∴ 0·125 gms. ... ... $\frac{1000 \times 0{\cdot}125}{5{\cdot}3}$ c.c. ...

$= 23{\cdot}6$ c.c. of $\left(\frac{N}{10}\right)$

Let the strength of H_2SO_4 soln. be 'S'

Then, 248 c.c. of (S) $H_2SO_4 \equiv 23{\cdot}6$ c.c. of $\left(\frac{N}{10}\right)$ Na_2CO_3.

Hence, $248 \times S = 23{\cdot}6 \times \frac{N}{10} = 2{\cdot}36 \times N$

Or, $S = \frac{2{\cdot}36}{248}(N) = 0{\cdot}0095(N)$

Therefore, the normality of the Sulphuric acid.
$= 0{\cdot}0095(N)$

and the wt. of it present in one litre
$= 0{\cdot}0095 \times 49$ gms.
$= 0{\cdot}4655$ gm.

(5) *What volume of normal acid will be required to completely neutralise 1 gm. of calcium carbonate which contains 4% sand as impurity ? (Atomic weight of calcium=40).* *Cal. Pre-U., 1965.*

Actual weight of $CaCO_3$ in gm. of the impure sample $= 1 - 0{\cdot}04 = 0{\cdot}96$ gm.

Now, 1000 c. c. of (N) acid contain 1 gm. eq. wt. of the acid and hence, will neutralise 1 gm. eq. wt. of $CaCO_3$

Eq. wt. of $CaCO_3 = \frac{40+12+48}{2} = \frac{100}{2} = 50.$

Hence, 50 gms. of $CaCO_3 \equiv 1000$ c.c. of (N) acid.

$\therefore$ 0'96......... $=\frac{1000}{50}\times 0'96$

$=19'2$ c.c. of (N) acid.

(6) *4'50 gms. of a dibasic acid was dissolved in water and the solution diluted to 500 ml. 20 ml., of this solution required 32 ml. of 1'25 N/10 alkali for neutralisation. Calculate the equivalent and molecular weight of acid.* *Cal. Pre-U., 1965.*

Let the strength of the soln. as prepared above be 'S'

Then, $20\times S=32\times 1'25$ N/10

Or, $S=\frac{32\times 1'25(N)}{20\times 10}=0'2$ (N).

Hence, 500 c.c. of 0'2 (N) soln. contain 4'50 gms. of the acid.

Or, $500\times 0'2$ c.c. of (N) soln............4'50 gms.............

Or. 100 c.c. of (N) soln. contain 4'50 gms. of the acid.

$\therefore$ 1000 c.c. of (N)...............45 gms......................

$\therefore$ the eq. wt. of the acid is 45.

(Since, by definition, 1000 c.c. of (N) soln. of any substance contain 1 gm. eq. wt. of the substance),

Again, we know

Eq. wt. of a substance$=\frac{\text{Mol. wt.}}{\text{Basicity}}$

Or, Mol. wt.=Eq. wt. × Basicity

Hence, the mol. wt. of the dibasic acid$=45\times 2=90$.

N. B. Similarly, the mol. wt. of a base

=Eq. wt. of the base × acidity.

The eq. wt. of a base being that wt. of the base which is neutralised by 1000 c.c. of (N) soln. of any acid.

Volumetric determination

Often it is necessary in the laboratory to find the strength of solutions especially those of acid and alkalis. It is usually carried out by **titration** which we discuss below.

The acid is placed in a long graduated tube called a burette and a definite volume, say 25 c. c. of caustic soda solution is placed in a flask by means of a pipette (fig. 129). A few drops of litmus solution is added to the caustic soda solution as an indicator.

By means of tap at the lower end of the burette, the acid is added drop by drop into the caustic soda solution. The solution remains blue until just a drop of acid turns it red. This is the end point. No more acid is added. The vol. of acid used is noted in the burette. Now if the strength of any one of the two solutions (acid and alkali) is known, the other can be found out.

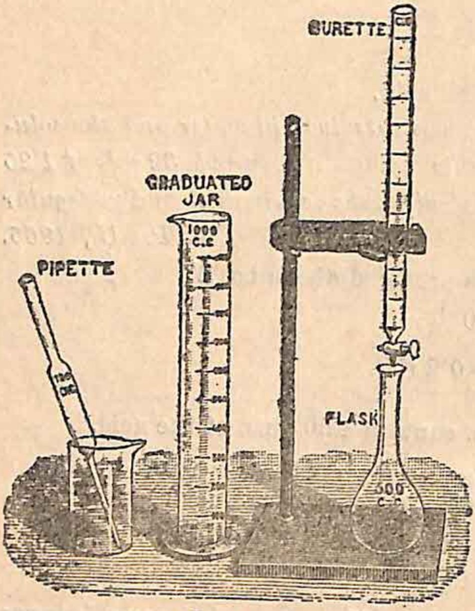


Fig. 129—Titration.

Suppose the strength of the acid is 0·12 (N) and its volume be 20·5 c.c. Let the strength of caustic soda be S.

Then we know,

$$V_1 \times S_1 = V_2 \times S_2$$

$$\text{or,} \quad 25 \times S = 20{\cdot}5 \times 0{\cdot}12\ (N)$$

$$\text{or,} \quad S = \frac{20{\cdot}5 \times 0{\cdot}12\ (N)}{25} = 0{\cdot}098\ (N)$$

Preparation of a Deci-normal solution of Sodium carbonate.

As Sodium carbonate can be obtained in a very pure state, a Normal or Deci-normal solution of it is used as the *starting-point* in Vol. Analysis, especially in Acidimetry and Alkalimetry.

Method—Take *pure* Sodium bi-carbonate in a platinum or porcelain basin and *very* carefully heat it, with constant stirring with a glass rod, so as not to allow it to fuse. After about 15 minutes, stop heating, cool the crucible in a desiccator and weigh it in a balance. Repeat the process of heating, cooling and weighing till the final *wt. is constant.* This shows that $NaHCO_3$ has been completely converted into Na_2CO_3. Now take a portion of the carbonate in a weighing-bottle. Exactly weigh out 5·3 gms. of Na_2CO_3 and put it in a *litre* flask. Add a little distilled water to the carbonate till it dissolves. Dilute the solution of Sodium carbonate, thus obtained, with more distilled water and thoroughly shake it. Now add more water and again shake the flask.

In this way, go on diluting the solution till the lowest edge of the *curved* surface (*meniscus*) of the solution stands just at the mark on the neck of the flask. Thus is prepared one litre of *strictly deci-normal* Na_2CO_3.

Preparation of Deci-normal Sulphuric acid

One litre of (N/10) H_2SO_4 will contain 4·9 gms of pure H_2SO_4. Now Sulphuric acid being a *liquid at the ordinary temp.* and *hygroscopic*, it is not possible to weigh out 4·9 gms. of the acid correctly. Then again, it is not *pure*. Ordinary H_2SO_4 (conc.) is never cent per cent H_2SO_4 ; it may contain 95 to 98 per cent of *real* acid. For our present purpose let us suppose it to contain 97 per cent of the *pure acid*. We see that 97 gms. of *pure* acid are present in 100 gms. of conc, H_2SO_4, Hence 4·9 gms. of the pure acid are present in.

$$97 : 4·9 : : 100 : x$$

$$\text{Or, } x = (4·9 \times 100) \div 97 = 5·051 \text{ gms. of } H_2SO_4 \text{ (conc.)}$$

It is, however, difficult to weight out 5·051 gms. of conc. H_2SO_4. We can measure it in an indirect way. Knowing that Mass = Volume × Density, we find that $5·051 = V \times 1·841$, where 1·841 is the density of Sulphuric acid, Or, $V = 5·051 \div 1·841 = 2·74$ c.c.

That is to say, 2·74 c.c. of H_2SO_4 contain 4·9 gms. of pure Sulphuric acid. We now measure out 2·8 c.c. of the acid by means of a *graduated* pipette in a *litre* flask and dilute it with water up to the standard mark, as in the case of Sodium carbonate solution above. Thus we have prepared *approximately*, but not strictly (N/10) H_2SO_4.

To make it strictly *deci-normal* we must titrate it with *strictly* (N/10) or (N) Na_2CO_3 sol or any other alkali.

N. B.—In like manner, we can prepare (N/10) HCl or (N/10) HNO_3.

Exercise.

1. 2 gms., 4 gms., 10 gms. and 25 gms of pure caustic soda are dissolved separately in enough water to make 500 c.c. of the solution. Find the normality of the solutions.

2. Find the amount of sodium carbonate present in (*a*) 10 c.c. (*b*) 30 c.c. (*c*) 125 c.c. of 0·25 (N) sodium carbonate solution.

3. 25 c.c. of sulphuric acid require 20 c.c. of 1·5 (N) caustic soda for complete neutralisation. Find the strength of the sulphuric acid.

4. 50 c.c. of caustic soda solution are mixed with 30 c.c. of (N) H_2SO_4 and the resultant mixture requires another 40 c.c. of $\left(\frac{N}{2}\right)$ H_2SO_4 for neutralisation. What is the strength of the caustic soda solution in normality and grams per litre ?

5. 100 c.c. of (N) HCl are mixed with 150 c.c. of caustic soda solution. The mixture requires 50 c.c. of 2 (N) H_2SO_4 for neutralisation. What is the strength of the caustic soda solution ?

6. 20 c.c. of (N) Na_2CO_3 solution is mixed with 30 c.c. of (N) HCl. Find the strength of the resultant solution. Is it acidic or alkaline ?

7. 25 c.c. of an alkali solution is mixed with 8 c.c. of a ·75 (N) acid solution, and for complete neutralisation it further required 15 c.c. of a ·8(N) acid solution. Find the strength of the given alkali solution. (*C. U., 1915.*) **[Ans =0·72 (N)]**

8. 1 gm. of *impure* Na_2CO_3 is dissolved in water and the sol. made up to 250 c.c. To 50 c.c. of this sol. 30·4 c.c. of 0·15 (N) HCl is added and the mixture required for neutralisation 50 c.c. of 0·12 (N) NaOH. Determine the strength of the impure carbonate sol. in terms of normality and also the p.c. of Na_2CO_3 in the *impure sample.* (*C. U., 1923.*) **[Ans. =0·0672 (N) ; 89·04%]**

9. A specimen of limestone contains 60% of $CaCO_3$. Calculate the amount of stone which will be required to generate just sufficient CO_2 to convert one litre of (N) NaOH sol, into Na_2CO_3. (*C. U., 1931*) **[Ans. = 83·3 parts by wt]**

10. 10 c.c. of HCl neutralise 40 c.c. of (N) NaOH. 1 gm. of chalk is dissolved in another 10 c.c. of the same HCl and the excess of acid required 20·5 c.c. of (N) NaOH for neutralisation. Calculate the percentage of $CaCO_3$ in the sample of chalk. **[Ans. =97·5%]**

11. 0·2815 gm. of $CaCO_3$ is dissolved in 30 c.c. of (N) HNO_3. The excess of acid requires 24·43 c.c. of (N) NaOH. Calculate the percentage of CO_2 in the sample of $CaCO_3$. (*All., 1928.*) **[Ans. =43·53%]**

12. 2·014 gms. of chalk were dissolved in 50 c.c., of (N) HCl, the excess of unchanged acid is titrated with (N) KOH, 10·7 c.c. being required. What is the percentage of $CaCO_3$ in the sample of chalk and what vol. of acid will be required to dissolve 20 gms ? (*U. P.*) **[Ans. =97·56% $CaCO_3$; 290·24 c.c.]**

13. 1·3456 grams of Na_2CO_3 are dissolved in water and the volume of the solution is made upto 250 c.c. 24·85 c.c. of a solution of sulphuric acid is required to just neutralise 25 c.c. of the Na_2CO_3 solution. Calculate the strength of the acid solution in terms of (*a*) normality and (*b*) grams per litre : (Na = 23, S = 32). *Cal. Pre-U., 1963.* **[Ans. =0·108 (N) : 5·574 gms / litre.]**

14. A solution of 0·53 gm. of sodium carbonate in 250 ml. of water is added to 1500 ml. of N/10 H_2SO_4 solution for partial neutralisation of the acid. Calculate the normality of the remaining sulphuric acid solution.

Cal., Pre-U., 1964. **[Ans. =0·08 (N)]**

15. 20 c.c. of a solution of sulphuric acid containing 24·5 gm. of acid per litre neutralised 15 c.c. of a solution of sodium hydroxide. What was (*a*) the normality of sodium hydroxide solution ; (*b*) the number of grammes of sodium hydroxide per litre of solution ? (H = 1, 0 = 16, S = 32, Na = 23).

Cal. Pre-U., 1966. **[Ans. = $\frac{2}{3}$ (N) ; 26·66 gms. / litre.]**

16. 0·125 gm. of anhydrous sodium carbonate was dissolved in water and it was found that 24·8 c.c. of a solution of sulphuric acid were required to neutralise it exactly.

Calculate (*a*) the normality of the acid ; (*b*) the weight in gms. of sulphuric acid present in one litre. *Cal. Pre-U., 1967.* **[Ans. = 0·09(N) , 4·77 gms. wt.]**

17. How do you prepare 500 c.c. of (N/2) Solution of Sodium Carbonate ?

Cal. Pre-U., 1961.

18. What do you understand by a Normal Solution of an acid ?

Cal. Pre-U. 1962.

19. 25 ml. of a soln. containing 6·6 gms. of a tribasic acid per litre neutralised 27·71 ml. of a soln. of 0·93 N/10 sodium hydroxide. Calculate the mol. wt. of the acid. *Cal. Pre-U. 1970.*

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GENERAL APPENDIX

For Easy and Quick Reference.

Alabanite, MnS.
Alabaster, $CaSO_4$, $2H_2O$—Highly crystalline and *natural* Calcium sulphate.
Alcohol (*Ethyl*), $C_2H_5(OH)$ ‖ Alcohol (*Methyl*). $CH_3(OH)$.
Alkhest—Universal solvent of the Alchemists Alkali *Marine*, Na_2CO_3, soda carb.
Alum, K_2SO_4, $Al_2(SO_4)_3$, $24H_2O$—Potassium Alaminium sulphate.
,, *ammonium*, $(NH_4)_2SO_4$, $Al_2(SO_4)_3$, $24H_2O$.
,, *natural*, K_2SO_4, $Al_2(SO_4)_3$, $Al_2(OH)_6$.
,, *Roman* -It is a Potash alum obtained from Alunite.
Alumina, Al_2O_3, Al-Oxide ‖ Alunite (alum-stone), K_2SO_4, $Al_2(SO_4)_3$, $4Al_2(OH)_3$ (*n*)
Amethyst (Violet), yakut, Al_2O_3 (*n*) ‖ Anthracite—C—Coal (*n*)
Antichlor—SO_2, Sulphur dioxide ‖ Apatite (*flwor*), $3Ca_3(PO_4)_2$, CaF_2 (*n*)
Aragonite—$CaCO_3$, $3MgSiO_3$—Rhombic variety of $CaCO_3$ (*n*)
Argentite—Ag_2S—Silver Sulphide (*n*) Argentum Vivum—Native Mercury.
Asbestos—$CaSiO_3$—Ca-Mg Silicate (*n*)
Auricome—H_2O_2, Hydrogen peroxide ‖ Austentite—a kind of hard steel.
Azurite—$2CuCO_3$, $Cu(HO)_2$. Basic carb. of Cu (*n*) ‖ *Aqua fortis*—Nitric Acid.
Aqua regia—conc. HNO_3 + conc. HCl in the prop. of 1 : 3.

Baking powder—a mix. of $NaHCO_3$ & Tartaric acid ‖ Baryta—BaO—Barium oxide.
Baryta water = $Ba(OH)_2$ sol.
Barytes—$BaSO_4$—Barium sulphate (*n*) ‖ Bauxite—Hydrated Al-oxide (*n*)
Benzene—C_6H_6—Hydrocarbon ‖ Beryl—$Al_2(SiO_3)_3$, $3BeSiO_3$. Al-Be Silicate (*n*)
Bittern—Mother-liquor from which common salt has crystallised out.
Black Ash—Mix. of Na_2CO_3, CaS and carbon.
Black Jack—ZnS—Zinc sulphide (*n*) ‖ Black lead—C—Graphite.
Bone-ash—$Ca_3(PO_4)_2$—Calcium phosphate ‖ Boracite, $2Mg_3B_8O_{15}$. $MgCl_2$ (*n*)
Borax—$Na_3B_4O_7$, $10H_2O$, Sodium pyroborate (*n*)
Borocalcite—CaB_4O_7, $6H_2O$, Calcium pyroborate ‖ Bort—C—Impure diamond.
Brimstone—S—Sulphur (*n*) ‖ Brine—strong solution of common salt in water.
Britannia metal—alloy of Sb, Sn, Cu, and Zn ‖ Bronze—Alloy of Cu and Sn.
Bronze (*aluminium*) alloy of Cu and Al, looking like *Gold*.

Calamine—$ZnCO_3$. Zinc carbonate (*n*) ‖ Calamine (*electric*), Zinc Silicate.
Calcite—$CaCO_3$, Calcium carbonate (*n*) ‖ Canton's phosphorus, CaS.
Calcspar—$CaCO_3$ (*n*) ‖ Caliche—Crude Chilinitre.

Calorizing.—It is a process similar to sherardizing except that Aluminium is used instead of zinc. The article (usually made of iron) is heated with Al-powder and Al_2O_3 in Hydrogen, whereby a surface consisting of Al_2O_3 followed successively by a layer of pure Alumininm and an alloy of Al-Fe is obtained.

Calx—oxide ‖ Calomel—Hg_2Cl_2—Mercurous chloride.
Carat—unit of wt. in the case of precious stone = ·235 gm.
Carbonado—C—impure diamond ‖ Carborundum—SiC, Silicon carbide.
Carnallite—$MgCl_2$, KCl, $6H_2O$—Double chloride of Mg and K (*n*)
Cassel yellow—$PbCl_2$, 7PbO—Basic lead chloride.
Cassiterite—SnO_2—Tin oxide (*n*) ‖ Celestine—$SrSO_4$—Strontium sulphate (*n*)
Cerussite—$PbCO_3$—Lead carbonate (*n*) ‖ Cinnabar—HgS—Mercuric sulphide (*n*)
Chalcopyrite—Cu_2S, Fe_2S_3, mixt., of Cu and Fe sulphides (*n*)
Coral—$CaCO_3$, Calcium carbonate (*n*) ‖ Corundum—Al_2O_3—Aluminium oxide (*n*)
Cryolite, AlF_3, 3NaF—Double fluroride of Al and Na (*n*) ‖ Chalk—$CaCO_3$.
Chili Saltpetre (*Chili nitre*),—$NaNO_3$—Sodium nitrate (*n*)
Corrosive sublimate—$HgCl_2$—Mercuric chloride ‖ Dephlogisticated air—oxygen.

Diaspore—Al_2O_3, H_2O—Hydrated Al—oxide (*n*) Dihydrol—H_2O_2.
Dolomite—$CaCO_3$, $MgCO_3$—Double carb of Ca and Mg (*n*)

Dowflake—Calcium chloride || Drier for paints—MnO_2, Mn-borate, etc.
Dutch *liquid*—$C_2H_4Cl_2$—ethylene chloride || Dutch *metal*—alloy of Cu and Zn.

Eau de Javelle—sol. of chlorine in cold dil. KOH sol.
Electrolytic gas—mix. of H and O as obtd. by the electrolysis of H_2O.
Emerald (*green*, Panna)—Al_2O_3 (*n*)
Epsom ralt—$MgSO_4$, $7H_2O$—Magnesium sulphate.

Felspar—K_2O, Al_2O_3, $6SiO_2$—Potassium Al—silicate (*n*)
Fire-clay—Aluminium silicate || Formaldehyde—HCHO.
Franklinite—ZnO, Fe_2O_3, $6MnO_2$—mix. of Zn, Mn and Fe-oxides (*n*)
Fluorspar—CaF_2—Calcium fluoride (*n*)

Glauber's salt—Na_2SO_4, $10H_2O$—Sodium sulphate.
Green vitriol—$FeSO_4$, $7H_2O$—Ferrous sulphate.
Galena—PbS—Lead sulphide (*n*) || Gangue—Impurities present in ores.
Garnets—Mg, Fe or Ba-Al-silicates || Guano—Sea-bird's excreta.
Gunpowder—mix. of Charcoal, Sulphur and Nitre.

Hausmannite—Mn_3O_4—Trimanganese tetroxide (*n*)
Haematite—Fe_2O_3—Ferric oxide (*n*)
Heavy spar—$BaSO_4$—Barium sulphate (*n*)
Horn blende—Aluminium silicate (*n*) || Horn Silver—AgCl—Silver chloride (*n*)
Hydrogenite—Al_2O_3, $3H_2O$—Hydrated Al-oxide.
Hydragilite—Mix. of Silicon, NaOH and Ca OH)$_2$.
Hydrolith—CaH_2—Calcium hydride || Inflammable air—H_2—Hydrogen.

Infusible white ppt.—HgCl (NH_2)—Mercuric Am-chloride.
Ivory black—Animal charcoal.

Kainite—K_2SO_4, $MgCl_2$, $MgSO_4$, $6H_2O$.
Kaolin—(*Kaolinite*). Al_2O_3, $2SiO_2$, $2H_2O$—Hydrated Al-silicate (*n*)
Kelp—Ash obtd. by burning sea-weed.
Kieselguhr—Silicious earth, remains of diatom (*n*)
Kiserite—$MgSO_4$, H_2O—Magnesium sulphate (*n*)

Lapis Lazuli (*ultramarine*)—mixture of sodium-Al-silicate and Na_2S.
Lipidolite—Lithium mica || Leucite, K_2O, Al_2O_3, $4SiO_3$—Potash-Al-Silicate (*n*)
Lignite—(*brown coal*)—A kind of coal.
Limonite—$2Fe_2O_3$, $3H_2O$—Hydrated iron oxide (*n*)
Lithopone—white paint—Mix. of $BaSO_4$ and ZnS.
Liver of sulphur (*Hepar sulph.*) obtd. by using S with K_2CO_3.
Loam—mixture of clay and sand || Luminous paint contains CaS, BaS, SiS or ZnS.
Lunar caustic—Silver nitrate || Laughing gas—N_2O—Nitrous Oxide.

Magnesia—MgO—Magnesium oxide || Magnestite—$MgCO_3$—Magnesium carbonate (*n*)
Magenetite—Fe_3O_4, Ferroso-ferric oxide.
Malachite—$CuCO_3$, $Cu(OH)_2$—Basic carbonate of Cu (*n*)
Manganin—alloy of Cu, Mn and Ni || Marcasite FeS_2—Iron disulphide.
Marl—mixture of clay and limestone.
Milk-of-lime—$Ca(OH)_2$—Suspension of $Ca(OH)_2$ in its solution.
Mosaic gold—SnS_2—Stannic sulphide.
Mohr's salt—Ferrous ammonium sulphate—$FeSO_4$, $(NH_4)_2SO_4$, $6H_2O$.

Nessler's reagent—Sol. of HgI_2 in KI sol. with excess of NaOH sol.
Nitre—KNO_3—Potassium nitrate.
Nitroglycerine (*Noble's oil*)—Glycerine trinitrate.

Olivine—Mg_2SiO_4—Magnesium silicate (*n*) || Opal—SiO_2—Silicon oxide (*n*)
Orpiment—As_2S_3—Arsenic trisulphide (*n*) || Orthoclase—Potash-Al-silicate (*n*)

Oxy-muriatic acid—Chlorine ‖ Oil of vitriol—H_2SO_4—Sulphuric acid.

Pearl ash—K_2CO_3—Potash-carb.
Perhydrol—strong sol. of H_2O_2 in water ‖ Periclase—MgO—Magnesium oxide.
Permanent white—$BaSO_4$—Barium sulphate ‖ Pewter—Alloy of Pb and Sb.
Pharaoh's Serpent—$Hg(CNS)_2$—Mercuric thiocyanate.
Phlogisticated air—N—Nitrogen.
Phosphor-bronze—Alloy of Cu and Sn containing P.
Plaster of Paris—$(CaSO_4)_2\ H_2O$—Calcium sulphate.
Platinized asbestos—Deposit of finely divided Pt. on asbestos.
Potash—K_2CO_3—Potassium carbonate.
Prussian blue—$Fe_4[FeCN_6]_3$, $9H_2O$—Ferric ferroyanide.
Purple of Cassius—Purple ppt. obtd. by adding $SnCl_2$ and $SnCl_4$ to $AuCl_3$ sol.
Pyrolusite—MnO_2—Magnanese dioxide (*n*).

Quartz—SiO_2—Silicon dioxide (*n*) ‖ Quicklime—CaO—Calcium oxide.
Quicksilver—Hg—Mercury.

Realgar—As_2S_2—Arsenic disulphide (*n*).
Resin of Copper—Cu_2Cl_2—Fused Cuprous chloride.
Red Prussiate of Potash—$K_3Fe(CN)_6$—Potassium ferricyanide.
Rouge—Fe_2O_2—Ferric oxide ‖ Sal Sedativum—H_3BO_3—Boric acid.

Sal Volatile—$(NH_4)_2\ CO_3$—Ammon. carb ‖ Saphire (*blue, neelum*) Al_2O_3.
Satin spar—$CaSO_4$, $2H_2O$—Fibrous Gypsum (*n*).
Selenite—$CaSO_4$, $2H_2O$—Transparent Gypsum (*n*).
Serpentine—Mg_3SiO_7, $2H_2O$—Mag. silicate hydrated (*n*).
Siderite—$FeCO_3$—Iron carbonate (*n*) ‖ Soluble glass—Na_2SiO_3 or K_2SiO_3.
Spathic iron ore—Iron carbonate (*n*).
Spelter—*Zn*—Impure commercial Zinc.
Spiegel—Alloy of Fe, Mn containing Carbon.
Spinel—$MgAl_2O_4$—Mag. aluminate (*n*).
Stibnite—Sb_2S_3—Antimony sulphide (*n*).
Sylvine—KCl—Potassium chloride.

Talc—$3MgSiO_3$, H_2O—hydrated Mag. silicate (*n*).
Tartar emetic—$2K(SbO)C_4H_4O_6$, H_2O—potassium antimony tartrate.
Tinstone—SnO_2—Tin oxide (*n*).
Topaz (*yellow*, pokraj or pusaparaj)—Al_2O_3 (*n*)
Tourmaline—Aluminium silicate (*n*).
Turnbull's blue—$Fe_3[Fe(CN)_6]_2$—Ferrous ferricyanide.
Turquoise—Al-Phosphate (*n*) ‖ Type metal—Alloy of Pb, Sb and Sn.

Ultramarine blue—Mix. of sodi-Al-Silicale Na_2S.

Venetain white—Mix. of White lead and $BaSO_4$.
,, red—Fe_2O_3, Ferric oxide ‖ Verdigris—Basic acetate of Copper.
Vemilion—HgS—Mercuric sulphide ‖ Vineagar—Dil. and impure Acetic acid.

Water glass—Thick solution of Sodium or Potassium silicate in water.
White lead—$2PbCO_3$, $Pb(OH)_2$—Basic carbonate of Pb.
Witherite—$BaCO_3$—Barium carbonate.
Wood's metal—Alloy of Bi, Pb, Sn and Cd.

Zinc-white—ZnO—Zinc Oxide.

(*n*)—means that the substance occurs *in nature*.